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(TITLE UNCLASSIFIED)
DEVELOPMENT OF PROPELLANTS
CONTAINING AN ENERGETIC OXIDIZER

T. P. Rudy
United Technology Center

TECHNICAL REPORT AFRPL-TR-67-236
July 1967

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UNCLASSIFIED FOREWORD

(U) This Fourth Technical Progress Report dated July 1967, under Contract No. AF 04(611)-10786, summarizes work performed during the period 1 June 1965 through 30 June 1967, by United Technology Center, Sunnyvale, California. The contract was initiated under Air Force Rocket Propulsion Laboratory, Research and Technology Division, Project No. 3059. For internal purposes, this report is designated UTC 2139-QTR4.

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(U) This report contains classified information extracted from the following documents: Final Technical Progress Report, Contract No. AF 04(611)-9894, August 1965; Final Report Contract No. AF 04(611) 10538, July 1966; Interim Engineering Progress Report, Contract No. AF 33(615)-2166, December 1966, Technical Report, Contract No. AF 04(611)11199, December 1966. These documents are classified CONFIDENTIAL, Downgrading Group 4.

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CONFIDENTIAL ABSTRACT

(C) United Technology Center(UTC) has conducted a program to improve and characterize the stability of propellants containing nitronium perchlorate (NP). Major emphasis was placed on the use of uncoated NP, UTREZ prepolymer (carboxy-terminated polyisobutylene), and NTEB crosslinker (a trifunctional aziridine). Reta-coated NP was employed in limited studies. Candidate plasticizers studied included nitroparaffins and paraffinic hydrocarbons. The most promising plasticizers were HMN (heptamethylnonane) and excess aziridine (NTEB and MAPO). Increased solids loadings without impairment of stability were obtained by control of NP particle size, use of ammonium perchlorate as a supplementary oxidizer, and use of increased concentrations of aluminum fuel. The increase of propellant life obtainable by storage at reduced temperatures was studied in detail. The most thermally stable formulations exhibited exotherms beginning below 150°C and culminating rapidly in ignition. All formulations, even under mild storage conditions, lost thermal stability at unacceptably high rates. The intrinsic stability of NP is regarded as inadequate to justify further effort with this oxidizer.

CONFIDENTIAL

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UTC 2139-QTR4

CONTENTS

<u>Section</u>		<u>Page</u>
I	INTRODUCTION	1
	1. Potential and Limitations of Nitronium Perchlorate	1
	2. Previous Accomplishments with NP	1
	3. Objectives of the Present Program	2
II	INGREDIENT STUDIES	5
	1. Binder Ingredients	5
	a. UTREZ Prepolymer	5
	b. Plasticizers	6
	c. Crosslinking Agents - Cure Catalysts	14
	2. Solid Ingredients	17
	a. Nitronium Perchlorate	17
	b. Ammonium Perchlorate	28
	c. Aluminum Fuel	28
	3. Summary of Ingredient Studies	28
III	FORMULATION STUDIES	31
	1. Crosslinker Concentration	31
	2. Solids Loading	33
	3. Summary of Formulation Studies	37
IV	EFFECT OF TEMPERATURE ON PROPELLANT STABILITY	43
	1. Propellant A (UTX-9118)	45
	a. Effect of Storage at Constant Temperature on Thermal Stability	45
	b. Effect of Prior Storage at Low Temperatures on Thermal Stability	49
	c. Deflagration and Explosive Combustion	53
	d. Mechanical Properties and Impact Sensitivity	54
	2. Propellant B (UTX-9171)	54
	a. Effect of Storage Temperature on Thermal Stability	54
	b. Deflagration	58
	c. Mechanical Properties	59
	3. Summary of Effect of Temperature on Propellant Stability	59

CONFIDENTIAL

CONTENTS (Continued)

<u>Section</u>		<u>Page</u>
V	MECHANISM OF NP PROPELLANT DEGRADATION	61
VI	SUMMARY AND CONCLUSIONS	63
	REFERENCES	67
	APPENDIX: Facilities	69

CONFIDENTIAL

UTC 2139-QTR4

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	(U) Effect of Normal Burning of UTX-9118-4, 63% Oxidizer, No AP	38
2	(U) Effect of Explosive Burning of UTX-9119-1, 68% Total Oxidizer, 20% AP	39
3	(U) Effect of Explosive Burning of UTX-9120-1, 93% Total Oxidizer, 22% AP	40
4	(U) Effect of Violently Explosive Burning of UTX-9121-1, 78% Total Oxidizer, 23% AP	41
5	(U) Effect of Temperature on Compatibility and Cure	44
6	(U) Storage Stability of Propellant A (UTX-9118-1) at Constant Temperature	47
7	(U) Effect of Prior Storage at 35°F on Stability of Propellant A (UTX-9118-2) at 10°F	51
8	(U) Effect of Prior Storage at Low Temperatures on Stability of Propellant A (UTX-9118-3) at Elevated Temperatures	52

CONFIDENTIAL

(This page is Unclassified)

TABLES

<u>Table</u>		<u>Page</u>
I	(U) Effect of Nitroparaffin Plasticizers on Viscosity of UTREZ	7
II	(U) Effect of MRPX Plasticizer on Propellant Stability	9
III	(U) Hydrocarbon Plasticizer Evaluation	10
IV	(U) Effect of Squalane Plasticizer on Propellant Stability	11
V	(U) Stability of Propellants Containing HMN Plasticizer	13
VI	(U) Stability of Propellants Containing MAPO	15
VII	(U) Stability of Propellants Containing MAPO and HMN	16
VIII	(U) Catalysis of the UTREZ/Aziridine Cure Reaction	18
IX	(U) Effect of Oxidizer Particle Size in a Relatively Unstable Formulation	20
X	(U) Effect of Oxidizer Particle Size in Relatively Stable Formulations	21
XI	(C) Hydrolysis of Reta-Coated NP	23
XII	(C) Properties of Reta-Coated NP	24
XIII	(C) Stability of Formulations Containing Reta-Coated NP	25
XIV	(C) Stability of Propellants Containing UTECOATED and Reta-Coated NP	27
XV	(U) Effect of Increased Crosslinker Concentration on Propellant Stability	32
XVI	(C) NP Propellants Containing AP and Aluminum	34
XVII	(C) Effect of AP and Increased Aluminum on Aging Stability of Propellants Containing Reta-Coated NP	35

CONFIDENTIAL

UTC 2139-QTR4

TABLES (Continued)

<u>Table</u>		<u>Page</u>
XVIII	(C) Stability of NP/AP Formulations at 60°F	36
XIX	(U) Stability of Propellants with Increased Solids Loadings	42
XX	(U) Thermal Stability of Propellant A (UTX-9118)	46
XXI	(U) Effect of Prior Low Temperature on Thermal Stability of Propellant A (UTX-9118)	50
XXII	(U) Combustion of Propellant A (UTX-9118-6)	55
XXIII	(U) Tensile Properties of Propellant A (UTX-9118-5)	56
XXIV	(U) Effect of Storage Temperature on Thermal Stability of Propellant B (UTX-9171)	57
XXV	(U) Tensile Properties of Propellant B (UTX-9171)	60
XXVI	(U) Propellant Formulations	65

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ABBREVIATIONS

AP	ammonium perchlorate
DSC	differential scanning calorimetry (performed using Perkin-Elmer DSC-1B instrument - sample size, 5 to 10 mg; heating rate, 10°C/min)
DTA	differential thermal analysis (sample size ca 50 mg; heating rate, 5°C/min)
HMN	2, 2, 4, 4, 6, 8, 8-heptamethylnonane
MAPO	tris - [1-(2-methyl)aziridiny]phosphine oxide
MRPX	A light, isoparaffinic oil obtained by special arrangement from Shell Oil Company
NP	nitronium perchlorate
NTEB	nitrilotriethyl- β -ethyleniminobutyrate
NTPB	nitrilotriethyl- β -propyleniminobutyrate
O/F	oxidizer-to-fuel (ratio)
TBM	tris-(butylenimino)melamine
TMAT	tris-(methylaziridinyl)triazine
TMPD	2, 6, 10, 14-tetramethylpentadecane
UTC	United Technology Center
UTREZ	carboxy-terminated polyisobutylene

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UTC 2139-QTR4

SECTION I

INTRODUCTION

1. POTENTIAL AND LIMITATIONS OF NITRONIUM PERCHLORATE

(C) The outstanding theoretical potential of NP as an oxidizer in solid propellants has been widely recognized for nearly a decade. Among the attractive properties of NP are: high oxygen content, favorable heat of formation, high density, lack of monopropellant character, and ease of synthesis by economical processes.

(C) On the other hand, NP's extreme hygroscopicity, limited thermal stability, and exceptional chemical reactivity have also been recognized.

(C) The balance of potential versus limitations has been such that numerous propulsion companies and government agencies have expended considerable effort to harness NP. In spite of heroic measures, some of which constitute the substance of this report, nothing approaching a practical NP propellant has been developed. It has been assumed generally: (1) that rigorous exclusion of moisture would circumvent the hygroscopicity problem, (2) that purification of NP and reduction of processing and storage temperatures would circumvent the thermal stability problem, and (3) that the extreme chemical reactivity of NP could be controlled by use of chemically resistant (compatible) ingredients, chemical passivators, and encapsulation. Because NP itself lacks apparent monopropellant or explosive character, it has been assumed that deterioration of the propellant would lead merely to ballistic unreliability stemming from porosity, impaired mechanical properties, and, perhaps, reduced autoignition temperature. As long as the oxidizer remains in the form of discrete particles, it has been assumed that mass transfer processes limit the worst possible interaction with the binder to an uncontrolled deflagration.

(U) It now appears that most of these assumptions are overoptimistic.

2. PREVIOUS ACCOMPLISHMENTS WITH NP

(C) Under Contract No. AF 04(611)-9894, UTC conducted a 12-month program to develop a curable binder containing a saturated-hydrocarbon difunctional polymer and to establish the compatibility of this binder with NP. A further objective of the program was ballistic characterization of the binder/NP formulation in small motors.

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(C) These objectives were achieved by the development of a system based on UTREZ prepolymer, MRPX plasticizer, and NTEB crosslinker (a tri-functional aziridinyl compound). Propellants containing both coated and uncoated NP were mixed, cast, and cured at room temperature. Those containing uncoated oxidizer were stable for only a few days at room temperature in a dry environment. Within 2 weeks, such propellants, even when unconfined, exploded shortly after ignition. Propellants containing Reta-coated oxidizer were found to be reasonably stable for periods up to 6 months under the same conditions. General characteristics of the propellants were insensitivity to impact and friction, sensitivity to moisture, limited thermal stability, and reasonable mechanical properties.

(C) All of the propellants were ballistically characterized in micromotor firings, and a formulation (UTX-7601) containing Reta-coated NP was tested in nominal 1-lb motor firings. Efficient oxidizer utilization, high burning rates, and moderately high pressure exponents were indicated by these tests. The most significant relationships were believed to be those derived from the 1-lb motors

$$r_b = 0.68 (P_c/1,000)^{0.49}$$

$$K_{st} = 320 (P_c/1,000)^{0.54}$$

3. OBJECTIVES OF THE PRESENT PROGRAM

(C) Initially the objective of the present contract was the development of practical propellants exploiting the high energy and favorable density of NP. This objective required significant improvement in the storage stability of the basic propellant system as well as the attainment of increased solids loadings.

(C) Since the most stable propellants developed previously were those containing Reta-coated NP, it was planned to emphasize use of this form of the oxidizer. In February, 1966, Union Carbide Corp. was in the process of preparing Reta-coated oxidizer for this program when 6 lb of coated and partly coated NP were destroyed in an explosion. This unprecedented event led to an intensive effort on the part of Union Carbide to determine the cause. The major physical factors responsible for the explosion have been established,^{(1)*} but details of the chemical processes remain to be determined.

* Parenthetical superscript numbers denote references on page 67.

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UTC 2139-QTR4

(C) Since only small samples of Reta-coated NP were available after the explosion, effort under the present contract was redirected. Major emphasis was placed on improvement and definition of the thermal and storage stability of propellants containing uncoated NP. Limited work was conducted to improve theoretical ballistic performance by increasing solids loadings.

(U) Unless otherwise specified, it is to be understood that all experimental work described in this report was conducted under atmospheres containing 5 ppm or less of water vapor.

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SECTION II

INGREDIENT STUDIES

(U) The following studies were directed toward propellant improvement by selection of ingredients and development of purification methods to increase thermal stability and permit attainment of increased solids loadings. The UTREZ/MRPX/NTEB binder developed under the previous program⁽²⁾ constituted a starting point for improvement.

1. BINDER INGREDIENTS

(C) Practical compatibility of the binder with NP depends not only on intrinsic chemical properties of the binder ingredients but also the maximum temperature required for processing the propellant. Low viscosity and high cure reactivity of the binder formulation are therefore desirable to minimize thermal exposure during mixing and curing.

a. UTREZ Prepolymer

(C) Under the previous program, considerable effort was expended to improve the compatibility of UTREZ prepolymer with NP. In the course of the present program it became apparent that compatibility was limited by the plasticizer and that further purification of the prepolymer held little promise of benefit.

(C) Fractions of the prepolymer differing in molecular weight were obtained by selective precipitation with various simple and mixed solvent systems. However, after purification, the various fractions differed little in respect to viscosity, cure reactivity, or compatibility with NP.

(U) Therefore, in the present program, work dealing with the prepolymer alone was limited to testing material produced in a pilot plant and purified in scaled-up equipment. The material is equivalent in performance to that previously produced in laboratory equipment and purified on a small scale. The scaled-up purification equipment described in the appendix was employed to purify approximately 5 lb of prepolymer for use in this program.

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(C) Of the possible means of decreasing viscosity of UTREZ binder, improved plasticization is particularly attractive. The relatively high viscosity of UTREZ at low temperatures (typically ca 2,500 poise at 25°C) is due only in part to its polyisobutylene backbone. Carboxyl-carboxyl association is believed to be an important factor. Evidence supporting this conclusion is the lower viscosity of hydroxy-terminated polyisobutylene and the extreme reduction of viscosity of UTREZ with increasing temperature (ca 13 poise at 95°C). Use of a polar plasticizer would be expected to decrease carboxyl-carboxyl association, and this expectation has been confirmed by experiments with polar compounds of low molecular weight. Unfortunately, most polar, but UTREZ-soluble, materials are either incompatible with NP or else they disrupt the crosslinking reaction with NTEB. However, nitroparaffins appeared to offer some promise, with the obvious benefit of providing additional oxidizer to the propellant. The latter benefit was considered desirable for improving O/F ratios.

(1) Nitroparaffins

(U) The effectiveness of several candidate nitroparaffin plasticizers is shown in table I. Although this limited study cannot be regarded as conclusive, it appears that a straight paraffin chain and terminal location of the nitro group are desirable. The nonlinear response of viscosity observed with the combination of 1-nitrobutane and MRPX (calculated viscosity, 500 poise; observed, 404 poise) is consistent with the desired interaction of the nitroparaffin with the carboxyl groups of UTREZ.

(U) Study of nitroparaffin plasticizers was terminated when it was found that available materials were severely depleted from propellants by volatilization during vacuum casting.

(2) Saturated Hydrocarbons

(C) MRPX isoparaffinic plasticizer was originally selected on the basis of apparent compatibility with NP and low volatility (boiling point above 700°F). However, continued studies showed that MRPX

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UTC 2139-QTR4

TABLE I

(U) EFFECT OF NITROPARAFFIN PLASTICIZERS
ON VISCOSITY OF UTREZ*

<u>Plasticizer</u>	<u>Viscosity at 25°C poise</u>
MRPX-1015, 15%w	658
1-Nitrobutane, 15%w	181
MRPX, 10%w/1-Nitrobutane, 5%w	404
2-Nitrobutane, 15%w	267
Nitrocyclohexane, 15%w	520
2,2-Dinitropropane	Insoluble

* UTREZ not purified

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contributed importantly to deterioration of the propellant. This is evident in the superior stability of propellant L (UTX-9146, no MRPX) compared to propellant D (UTX-9118, MRPX 15% w of binder) as shown in table II. Furthermore, when it became obvious that no propellant containing NP could survive temperatures appreciably above ambient, the requirement for very low volatility disappeared. Therefore, other saturated hydrocarbons of lower molecular weight were evaluated for plasticizing efficiency and NP compatibility, and the results are shown in table III. Candidate plasticizers were purified prior to use by the usual sequence of treatments; sulfuric acid extraction, water washing, dissolution in carbon tetrachloride followed by exposure to fuming nitric acid, water washing, drying over anhydrous sodium sulfate and then by passage through a column of silica gel, vacuum distillation, and, finally, drying over phosphorus pentoxide.

(C) On the basis of spot plate tests, squalane appeared to be more compatible with NP than MRPX. However, in propellant formulations this proved not to be the case (table IV).

(C) The branched paraffin TMPD was found to be a more effective plasticizer than MRPX, but in spot plate tests it caused rather rapid discoloration of NP. However, since the TMPD itself did not develop color for 9 days, it appeared that a residual impurity might be responsible for the initial reaction. When exposure to NP was employed as part of the purification procedure and the treated TMPD was tested with fresh NP, the initial discoloration of NP did not occur.

(C) Studies at Midwest Research Institute⁽³⁾ showed that the products of interaction of NP with hydrocarbons are apparently largely confined to the oxidizer-hydrocarbon interface. This observation and the favorable result previously cited led to further experiments to establish the value of treatment with NP to purify TMPD.

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TABLE II

(U) EFFECT OF MRPX PLASTICIZER ON PROPELLANT STABILITY

Sample UTX-	D 9118-4	L 9146-1
Composition		
NP, 30-40 mesh, %w	63	65
Al, 35 μ , %w	2	0
Binder, %w	35	35
UTREZ, equiv.	1.0	1.0
NTEB, equiv.	1.2	1.2
MRPX, %w of binder	15	0
Storage temp., $^{\circ}$ F	60	60
DTA		
Exotherm, $^{\circ}$ C/ ignition, $^{\circ}$ C at age, days		
3	67/78	69/81
5	69/80	---
7	64/80	72/81
11	63/80	76/87
15	66/79	72/83
20	61/78	65/80
25	59/77	---
30	60/75	65/80
35	59/75	66/78
40	50/74X*	66/80
50	---	66/78
60	--	60/76
70	---	61/78
80	---	58/78X
90	---	62/74X

* X = Explosion

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TABLE III
(II) HYDROCARBON PLASTICIZER EVALUATION

<u>Plasticizer (15%w in UTREZ)</u>	<u>Viscosity Poise</u>	<u>NP Compatibility of Plasticizer</u>
With purified UTREZ		
MRPX-1015 ^{a)}	847 at 30°C	Color, 1 week
Humble Marcol 70 ^{b)}	660 at 30°C	(Not tested)
Humble Marcol 72 ^{b)}	575 at 30°C	Color, 5 min.
Shell Spray Baas ^{c)}	330 at 23.5°C	Color, 2 hr.
With unpurified UTREZ		
MRPX-1015	658 at 25°C	Color, 1 week
Squalane	945 at 23°C	Color, > 1 week
TMPD ^{d)}	550 at 23°C	Color, 9 days ^{f)}
HMN ^{e)}	< 550 at 23°C	Color, > 2 weeks

- a) Experimental isoparaffinic oil
b) Commercial white oil
c) Hydrotreated petroleum raffinate, bp 185°-200°C
d) 2, 6, 10, 14-tetramethylpentadecane
e) 2, 2, 4, 4, 6, 8, 8-heptamethylnonane
f) Although TMPD developed color only after 9 days, the NP was discolored after one day.

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TABLE IV

(U) EFFECT OF SQUALANE PLASTICIZER
ON PROPELLANT STABILITY

Composition	Formulation			
	UTX- 8166	UTX- 8167	UTX- 8168	UTX- 8169
Plasticizer, 15%w of binder	MRPX	Squalane	MRPX	Squalane
Total binder, %w	25	25	25	25
NP, 30-40 mesh, UTEKOATED, %w	59	59	41.3	41.3
AP, ground %w	0	0	17.7	17.7
Al, %w	16	16	16	16
Impact Sensitivity 4 days, kg cm	27	28	>36	33
DTA Exotherm, °C/ ignition, °C at age, days				
3	72/90	64/79	73/90	72/86
7	65/87	64/82	65/82	64/83
10	59/80	54/77	60/81	58/80
11	60/78	46/74	61/78	48/78
Combustion, unconfined, 11 days	Normal	Explosive	Stable	Explosive

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(C) A 2.5-g sample of TMPD was placed in contact with 0.15 g of 30-to-40-mesh NP in the dry box. After 7 days at ambient temperature, the NP appeared sticky, but not discolored. On the ninth day of contact, a slight yellowing of the TMPD was observed. After 13 days, both the NP and the TMPD showed a brown discoloration. At intervals during the treatment period, small samples of TMPD were removed and incorporated in propellant formulations containing uncoated NP. All the formulations were stored at ambient temperature. Within 3 to 4 days, all but one propellant sample had visibly deteriorated (swelled). The formulation containing TMPD which had been treated for 9 days survived 6 days before swelling was evident. On the basis of this study, TMPD was eliminated as a candidate plasticizer, and the use of NP in the purification procedure was explored no further.

(U) The plasticizer HMN exhibited excellent compatibility in spot plate tests. Its volatility caused some concern initially, but studies simulating vacuum casting revealed less than 0.1% weight loss when a binder formulation containing 15% w HMN was held under vacuum for 40 minutes. Propellants containing HMN compared favorably in stability with an unplasticized formulation as shown in table V. Note that these formulations contained 2.0 equivalents of NTEB crosslinker, which contributes to stability. Further experiments with HMN are discussed in subsequent paragraphs in connection with the use of MAPO.

(3) MAPO

(C) Most formulators have observed that MAPO increases the fluidity and processability of propellants. Although MAPO is ordinarily employed as a crosslinking agent for carboxy-functional binders, it reacts very slowly at the low temperatures required for safe processing of NP propellants. Furthermore, in competition with a crosslinking agent as reactive as NTEB, MAPO participates little in the initial cure. Distilled MAPO polymerizes in the presence of NP but is otherwise quite compatible. In fact,

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TABLE V

(U) STABILITY OF PROPELLANTS
CONTAINING HMN PLASTICIZER

<u>Sample</u>	<u>109-4</u>	<u>5%HMN</u>	<u>10%HMN</u>
NTEB equiv.	2.0	2.0	2.0
NP, 30-40 mesh, %w	63	60	60
HMN, %w of binder	none	5	10
Storage temp.	ambient	ambient	ambient
DTA Exotherm, °C/ ignition, °C <u>at age, days</u>			
1	80/94	78/88	71/86
5	82/92	---	---
6	---	72/87	77/86
7	76/88	---	---
10	---	70/81	75/89
12	73/86	---	---
14	74/90	---	---
16	---	72/81	69/82
19	66/80	---	---
20	---	65/81	69/82
21	67/82	---	---
23	64/84	---	---
24	---	71/83	64/81
26	64/82	---	---
28	66/82	---	---
30	66/82	71/84	66/84

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MAPO appears to stabilize NP propellants. Therefore, MAPO alone and in combination with HMN was evaluated as a potential stabilizing plasticizer with the encouraging results shown in tables VI and VII. Of course, the use of MAPO raises the prospect of postcuring of the propellant. However, postcuring of test propellants was not observed. The most stable propellant containing uncoated NP prepared in this program is MS 210-125-3 (no HMN, MAPO 10%w of binder; see table VII). Work with MAPO and HMN was terminated when the generally poor prospects for development of practical NP propellants led to cessation of work with this oxidizer.

c. Crosslinking Agents - Cure Catalysts

(C) In the preceding program NTEB proved to be superior to a variety of polyfunctional aziridinyll compounds in terms of both intrinsic compatibility with NP and cure reactivity with UTREZ. However, the study of candidate crosslinkers was not exhaustive. It appeared possible that even better curatives could be developed.

(C) Earlier studies indicated that TMAT is attractive with respect to cure reactivity and NP compatibility. However, the limited solubility of TMAT in UTREZ and MRPX at low temperatures have precluded its use. Studies were conducted to find a solubilizing agent for TMAT which is acceptable for use in the propellant. At room temperature, nitroparaffins and relatively nonpolar organic compounds do not dissolve TMAT. A variety of polar organic materials (alcohols, ketones, etc.) are effective solvents, but these are incompatible with NP. Chloroform and several other halogenated hydrocarbons of low molecular weight appeared promising, but these compounds can be used only in low concentrations if ballistic performance is to be maintained. Furthermore, these solvents are quite volatile and would be expected to escape from the propellant even at reduced temperatures.

(U) Use of 15%w chloroform in UTREZ is required to dissolve TMAT. In accelerated testing (60°C) the gel time was found to be 15.6 hours compared to 7.2 hours for NTEB at an aziridine/carboxyl ratio of 1.3:1.0.

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TABLE VI

(U) STABILITY OF PROPELLANTS CONTAINING MAPO

Sample	I-A	I-B	I-C	II-A	II-B	II-C
NTE8, equiv.	2.0	2.0	2.0	2.5	2.5	2.5
NP, mesh size	30-40	8-20	8-20 crushed	30-40	8-20	8-20 crushed
DTA Exotherm, °C/ ignition, °C at age, days						
1	85/93	87/96	86/94	95/100	86/96	89/100
3	83/96	81/93	79/91	83/90	95/102	83/91
7	72/87	72/87	71/86	88/95	77/90	73/90
13	67/84	75/87	76/84	76/91	78/88	70/84
21	72/84	74/83	72/82	69/83	68/85	70/79
27	70/85	70/84	67/83	70/82	70/85	69/82
31	73/84	78/93	71/84	69/87	77/90	76/86
35	69/85	72/88	74/85	69/85	77/91	68/82
41	74/90	77/92	73/84	---	---	---
49	77/90	---	---	---	---	---

*-Propellant composition: NP, 60%w; binder, 40%w;
MAPO, 5%w of binder. Storage at 75°F

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TABLE VII

(U) STABILITY OF PROPELLANTS
CONTAINING MAPO AND HMN*

<u>Sample</u>	<u>MS 210- 125-1</u>	<u>UTX- 9175-1</u>	<u>MS 210- 125-2</u>	<u>MS 210- 125-3</u>	<u>MS 210 125-4</u>
NTEB, equiv.	2.0	2.0	2.0	2.0	1.5
NP, 8-20 mesh, %w	63	63	63	63	63
MAPO, %w of binder	---	---	5	10	---
HMN, %w of binder	10	10	5	---	10
Cure time at 75°F, days	8	8	12	15	8
DTA					
<u>Exotherm, °C/ ignition, °C at age, days</u>					
1	82/95	---	79/86	86/98	73/83
3	76/90	---	82/94	85/99	76/86
7	81/92	84/93	82/90	90/101	77/87
9	76/91	---	89/100	93/103	78/94
14	73/89	77/91	85/94	90/103	71/86
16	71/86	---	70/91	88/101	73/83
22	77/88	73/87	74/86	77/91	67/83
27	74/85	---	72/86	76/90	71/85
34	---	67/85	---	77/92	---
38	---	67/85	---	76/90	---
42	---	74/85	---	71/86	---
48	---	68/87	---	77/86	---
55	---	68/87	---	70/92	---
59	---	---	---	72/88	---
66	---	---	---	66/89	---
70	---	---	---	68/92	---
97	---	---	---	+	---

* Storage at 75°F

+ Sample apparently stable, did not soften or gas.

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(U) Limited study was conducted to find means of catalyzing the crosslinking reaction of carboxyl groups with aziridines. Use of certain metal salts and chelates appeared promising.

(U) Preliminary studies showed that both zirconium acetyl-acetonate and chromium 2-ethylhexanoate catalyze the reaction of carboxyl groups with certain aziridines. The latter catalyst is particularly effective with UTREZ (table VIII).

(C) Studies of the use of catalysts in propellant formulations containing NP had not yet been conducted at the time of the decision to discontinue work with this oxidizer.

2. SOLID INGREDIENTS

a. Nitronium Perchlorate

(C) It was originally intended to perform most of the propellant development work in this program using Reta-coated NP. However, when coated oxidizer became unavailable, emphasis was shifted to the use of uncoated material. It was hoped that high-purity NP would become available as a result of work at Esso Research and Engineering Co. under Air Force Contract No. AF 04(611)-10538.⁽⁴⁾ However, this did not come to pass. Therefore, studies were confined to material produced by Callery Chemical Co. The 30-to-40 mesh oxidizer used in this program had been prepared at Thiokol Chemical Co. from Callery's NP fluff by compacting, grinding, and sieving. The 8-to-20-mesh oxidizer was prepared by compacting, crushing, and sieving at Callery. All NP used in the present study was vacuum-treated at 10^{-5} torr for at least 16 hours at ambient temperature prior to use (appendix).

(C) Late in the present program, DSC with effluent gas detector became available and was employed to study individual ingredients as well as complete propellant formulations. Tests of uncoated, 8- to -20-mesh NP revealed a thermal event which apparently has not been reported previously. At 54°C, a gas (possibly oxygen) with higher thermal conductivity than nitrogen begins to be evolved. At 57°C, an endotherm is first detected. This endotherm is presumed to be associated with gas evolution. The remainder of the thermogram is consistent with previous DTA studies of NP, i.e., an endotherm at 143°C peaking at 146°C, followed by an exotherm starting at 150°C accompanied by extensive gas evolution.

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TABLE VIII

(U) CATALYSIS OF THE UTREZ/AZIRIDINE CURE REACTION^(e)

<u>Aziridine Curative</u>	<u>COOH/Imine Equivalence Ratio</u>	<u>Chromium 2-Ethylhexanoate %w</u>	<u>Gel Time 60°C, hr</u>
NTEB	1.1	1	3.5
NTEB	1.1	0	4.8
NTPB ^(b)	1.1	1	15.8
NTPB	1.1	0	23.3
TBM ^(c)	1.1	1	21.5
TBM	1.1	0	40.1

- (a) All gumstock formulations contain 15%w MRPX plasticizer
(b) Nitrilotriethyl- β -propyleniminobutyrate
(c) Tri-(butylenimino)melamine

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(U) In the previous program, endotherms were observed at 52°C when relatively large samples of propellants containing Reta-coated oxidizer were heated in an oven. It was noted at the time that this endotherm was not apparent in DTA tests. Evidently the DTA apparatus is insufficiently sensitive to detect this event.

(C) The implication of instability of NP at such a low temperature is clear and discouraging. The gap between ambient temperature and the temperature at which NP by itself exhibits instability has been reduced from the previously assumed value of at least 35°C to a mere 25°C.

(1) Nitronium Perchlorate Particle Size

(C) Since the initial reactions leading to degradation of NP propellants appear to occur mainly at binder-oxidizer interfaces, reduction of interfacial areas by use of coarse oxidizer would be expected to promote stability. Of course there are important factors limiting the maximum practical size of oxidizer particles. Some of these factors are processability, mechanical properties of the propellant, and, especially, combustion efficiency.

(C) In relatively unstable propellant formulations, the coarse oxidizer does afford improved stability (table IX). However, there is little difference between coarse and fine NP (tables VI and X) in more stable formulations. These results suggest a secondary deterioration process not confined to the oxidizer-binder interface.

(2) Reta-Coated NP

(C) Under this contract, work with Reta-coated NP was not extensive. Initially the only Reta-coated oxidizer available was that remaining from the previous program.

(C) Studies conducted with this oxidizer have conclusively shown that the coating deteriorates even when stored in an atmosphere containing 5 ppm or less of moisture and at a temperature of 28°C. A sample of 30-to-40 mesh NP with 4.4%w Reta coating (7402-66-5), which had been stored under the indicated

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TABLE IX

(U) EFFECT OF OXIDIZER PARTICLE SIZE
IN A RELATIVELY UNSTABLE FORMULATION*

Sample <u>UTX-</u>	AID <u>9118-6</u>	M <u>9147-1</u>
NP particle size, mesh	30-40	8-20
DTA Exotherm, °C/ ignition, °C <u>at age, days</u>		
6	68/82	72/84
8	64/77	70/84
10	59/76	62/78
13	52/74X [†]	66/82
15	62/73	62/79
17	48/72	55/74
21	58/76X	60/76
22	55/79	56/74X
24	62/76	60/78

* Formulation: NP, 63%w; Al, 2%w, binder, 35%w;
NTEB/UTREZ equiv. ratio, 1.2; MRPX, 15%w of binder.
Storage at ambient temperature.

[†] X = Explosion

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UTC 2139-QTR4

TABLE X
(U) EFFECT OF OXIDIZER PARTICLE SIZE
IN RELATIVELY STABLE FORMULATIONS

Sample UTX-	N 9163	O 9166	109-1	109-2	109-3	109-4	109-5	109-6	109-7	109-8
Composition										
NP, uncoated 30-40 mesh, %w	63	---	---	65	---	63	---	65	---	63
8-20 mesh, %w	---	63	65	---	63	---	65	---	63	---
Al, 35 μ , %w	2	2	0	0	2	2	0	0	2	2
Binder*, 35%w										
UTREZ, equiv.	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
NTEB, equiv.	2.0	2.0	2.0	2.0	2.0	2.0	2.5	2.5	2.5	2.5
DTA Exotherm, °C/ ignition, °C at age†, days										
1	---	---	76/86	83/97	74/86	80/94	80/92	88/100	70/80	84/98
3	87/98	76/88	---	---	---	---	---	---	---	---
5	78/92	74/87	78/92	74/87	80/90	82/92	74/88	76/91	82/96	74/85
7	73/86	74/87	72/84	75/90	76/88	76/88	76/89	76/88	78/88	81/95
9	66/78	66/80	74/90	69/84	74/90	72/88	76/89	76/92	78/97	80/94
12	64/86	66/86	74/88	74/87	76/90	73/86	74/88	76/88	76/88	76/90
15	63/83	62/79	72/90	74/89	71/86	74/90	76/92	74/92	73/91	73/90
20	68/83	65/80X**	68/84	71/85	71/85	66/81	69/85	71/86	72/87	70/84
25	68/80	69/83	65/84	71/82	65/84	64/83	69/36	68/83	70/85	67/82
30	64/80	66/80	71/87	66/83	66/84	66/82	69/83	73/86	72/86	70/84
35	---	---	---	---	69/86	66/80	---	---	72/85	---
40	---	---	---	---	68/84	70/84	---	---	71/85	---
50	---	---	---	---	71/87	67/82	---	---	84/87	---
60	---	---	---	---	64/88	73/86	---	---	74/90	---
70	---	---	---	---	69/83X	70/85	---	---	74/90	---
80	---	---	---	---	---	60/82X	---	---	72/90	---
90	---	---	---	---	---	---	---	---	62/82	---

* No plasticizer present

† Storage at ambient temperature

** X = Explosion

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conditions for ca 15 months, gassed within 20 hours of first contact with a standard binder formulation. Another sample of coated oxidizer (7402-123-5A) differing only in age (9 months) gassed in 9 days. Still another sample (402-123-5) of 9 months' age which had been stored at a fluctuating but lower average temperature gassed after 1 month. Microscopic examination of the poorest sample of Reta-coated NP revealed obvious deterioration and flaking of the coating. Interestingly, DTA of this sample of oxidizer showed an ignition temperature of 113°C compared with 96°C for the best sample. A possible explanation of this behavior is that extensive nitration of the deteriorated coating rendered it less reactive with NP.

(C) One year after their coating, the better samples were tested for hydrolysis after water immersion. Results are shown in table XI. The harmful effect of coating deterioration on propellant stability is discussed more fully in section III, 2.

(C) Late in the present program, samples of freshly coated NP were obtained from Union Carbide. Properties and results of both DTA and DSC are shown in table XII. These samples also exhibit the low temperature endotherm and accompanying gas evolution found with uncoated NP. However, the temperature at which this process is detectable increases with decreased surface area and with increased thickness of Reta coating.

(C) Propellants were prepared using the new Reta-coated NP samples in a relatively stable binder formulation. Storage stability of these samples at ambient temperature is compared in table XIII with that of a comparable formulation containing uncoated NP. It is evident that Reta coating provides a marked improvement in initial stability but that this advantage diminishes considerably with time. Furthermore, the initial superiority of very thick coatings almost disappears during storage. This may be a manifestation of the transport of NP through the coating by the process suggested by investigators at Midwest Research Institute.⁽³⁾

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TABLE XI

(C) HYDROLYSIS OF RETA-COATED NP^(a)

<u>Hydrolysis</u>	<u>Sample 7405-123-5</u>	<u>Sample 7405-123-5A</u>
Original value, ^(b) 7 hr immersion in H ₂ O	<1%	<1%
Aged 1 year		
1-1/2-hr immersion	39%	87%
3-hr immersion	52%	93%

(a) 30-40 mesh, 4.4%w coating

(b) Determined by Union Carbide immediately after coating

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TABLE XII

(C) PROPERTIES OF RETA-COATED NP

Sample	Mesh Size	% Reta-D	% Reta-C	% Reta Total	DTA
					Exotherm/ Ignition°C
8361-89	8-20	1.65	2.65	4.30	82/106
8361-91	8-20	2.55	5.20	7.75	81/106
8361-87	30-40	2.75	5.70	8.45	86/103
8361-83	30-40	1.80	1.60	3.40	86/103
Uncoated	8/20	----	---	---	150/---

	DSC			
	Endotherms, °C		Exotherms, °C	
	Onset/Peak	Onset/Peak	Onset/Peak	Onset/Peak
8361-89	66/87	144/147	103/121	152/177
8361-91	59/87	143/146	100/125	150/176
8361-87	51/88	143/145	95/120	146/176
8361-83	51/64	143/145	77/120	146/163
Uncoated	57/87	143/146	---	150/---

	Gas Evolution Events*, °C		
	A	B	C
8361-89	70	112	155
8361-91	64	105	154
8361-87	55	110	163
8361-83	54	105	151
Uncoated	54	---	155

- *Events: A. First evidence of gas, thermal conductivity suggests O₂.
 B. Probably products of oxidation of Reta.
 C. Beginning of major decomposition of NP.

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UTC 2139-QTR4

TABLE XIII

(C) STABILITY OF FORMULATIONS CONTAINING RETA-COATED NP

Formulation <u>UTX-</u>	<u>9171</u>	<u>10000</u>	<u>10001</u>	<u>10002</u>	<u>10003</u>
UTREZ (1.0 equiv.)%w	26.59	22.52	24.44	24.90	22.15
NTEB (2.0 equiv.)%w	8.41	7.13	7.73	7.88	7.00
Al, 35 μ , %w	2.00	2.00	2.00	2.00	2.00
NP, %w	63.00	68.35	65.83	65.22	68.85
Mesh size	8-20	8-20	8-20	30-40	30-40
Reta, %w	none	7.75	4.3	3.4	8.45
DTA					
Exotherm, $^{\circ}\text{C}/$					
ignition, $^{\circ}\text{C}$					
<u>at age, days</u>					
0	---	93/107	94/111	90/104	92/106
3	74/86	96/109	97/112	91/104	92/107
6	78/87	91/106	96/111	90/102	93/106
9	---	89/105	87/101	83/96	87/103
13	71/87	90/108	92/109	85/99	83/98
16	---	88/101	93/108	80/93	89/103
20	75/92	89/107	89/107	82/96	86/104
23	77/91	82/97	79/93	75/90	85/99
27	72/88	34/97	79/94	75/89	87/102
31	77/90	84/99	82/95	76/89	80/97
36	74/90	81/94	79/92	76/89	80/93
43	77/90	84/99	80/93	71/85	86/100
45	74/92	86/100	93/108	69/83	73/88
50	---	85/98	84/95	75/85	78/89
57	71/90	80/93	84/98	74/87	83/97
64	69/88	79/91	87/101	70/83	76/90
71	69/86	84/99	86/105	69/86	75/87
78	68/85	79/93	79/93	74/85	76/88
85	67/85	76/89	76/89	75/87	81/95
92	67/84	81/94	74/89	73/86	75/88
98	69/85	80/91	83/94	---	---

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(C) At the conclusion of the foregoing study, it was observed that the binders of propellants UTX-10002 and 10003 (30-to-40-mesh Reta-coated NP) had lost elasticity and would crumble under pressure. Furthermore, bonding to the oxidizer had been lost. Although propellants UTX-10000 and 10001 (8-to-20-mesh Reta-coated NP) had not lost elasticity, bonding to the oxidizer had diminished significantly.

(3) UTECOATING

(C) During the period that Reta-coated NP was not available, a limited study of the utility of UTECOATING was undertaken. Batches of UTECOATED 30-to-40-mesh NP were prepared for evaluation in propellant formulations. Typical coating levels were 0.8%w (gravimetric determination) or 1.0%w to 1.4%w (hydrolysis followed by acidimetric titration). Behavior of UTECOATED NP under DTA differed little from that of uncoated NP. No significant effects were observed at temperatures below 135°C. At this temperature, an endotherm began and peaked at ca 145°C. A major exotherm began at 163°C and peaked at ca 175°C. In contrast, Reta-coated NP (4.4%w) exhibits an exotherm beginning in the range 75° to 90°C and culminating in ignition at 95° to 115°C. Undoubtedly, a major factor in the difference between UTECOATED and Reta-coated oxidizer is the greater fuel content of the heavier Reta coating.

(C) Comparison of the stability of propellants containing UTECOATED NP with one containing the best available, but nonetheless deteriorated, Reta-coated oxidizer is shown in table XIV. The favorable initial stability of the formulations with UTECOATED NP is actually inferior to that of formulations containing fresh Reta-coated NP (see table XIII). Furthermore, the propellants with UTECOATED NP deteriorated rapidly and probably reached an explosive state in less than 2 weeks. The apparent recovery in thermal stability after 2 weeks is deceptive. Visible degradation continued and explosive character persisted.

(C) UTECOATING appears to offer little promise of stabilizing NP propellants.

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TABLE XIV

(C) STABILITY OF PROPELLANTS CONTAINING
UTE COATED AND RETA-COATED NP

Composition	Formulation		
	<u>UTX-8170</u>	<u>UTX-8172</u>	<u>UTX-8171</u>
Binder [*] , %w	25	25	25
Al, 35 μ , %w	16	16	16
NP, 30-40 mesh			
UTE COAT-M, ca 0.8%w	59%w	---	---
UTE COAT-N, ca 0.8%w	---	59%w	---
Reta [†] , 4.4%w	---	---	59%w
DTA			
Exotherm, °C/ ignition, °C at age, days			
4	74/86	74/86	53/74
6	68/83	62/84	53/75
10	55/76	56/77	62/81
12	49/72	52/74	63/81
13	49/75	49/74	62/82
19	64/84	64/83	66/83
25	76/90	75/89	74/89
46	75/89	74/90	74/89
Combustion, unconfined			
25 days	Explosive	Explosive	Normal
46 days	Explosive	Explosive	Normal

* - NTEB/UTREZ equiv. ratio, MRPX, 15%w of binder.

† - Sample one year old; coating deteriorated.

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CONFIDENTIAL**b. Ammonium Perchlorate**

(C) Two considerations led to the study of finely divided AP as a supplementary oxidizer to increase solids loading. First, the probability that the stability of NP propellants varies inversely with oxidizer-binder interfacial area militates against the use of fine NP. Second, the smallest particle size of NP which can be Reta-coated practically is 30 to 40 mesh. Furthermore, the weight of coating required for given protection increases according to surface area of the oxidizer and becomes ballistically prohibitive with NP of smaller particle size.

(C) Experiments with formulations containing AP are discussed in detail in section III, 2 (Formulations Studies, Solids Loading). In general, AP appeared to have no adverse effect on the thermal stability of NP propellants, but by permitting formulations of more stoichiometric mixtures, it contributed to the violence of explosive combustion.

c. Aluminum Fuel

(C) In the previous program, aluminum contents of propellants did not exceed 3.5%w. Because the maximum theoretical specific impulse of the NP/UTREZ/Al system requires an aluminum content of 15%w, formulation studies in this region were conducted. No adverse effects on propellant properties were observed as the result of using 35 μ -spheroidal aluminum in concentrations up to 16%w. Furthermore, no differences in propellant stability were observed when the aluminum was untreated, oven dried, or vacuum dried. Results of propellant stability studies are discussed in section III, 2 (Formulation Studies, Solids Loading).

3. SUMMARY OF INGREDIENT STUDIES

(U) Fractionation of UTREZ on the basis of molecular weight offers no improvement in compatibility or processability.

(U) Nitroparaffins effectively plasticize UTREZ, but available types are unacceptably volatile.

(U) Of a variety of hydrocarbon plasticizers tested, only HMN appears superior to MRPX.

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- (C) Treatment of plasticizers with NP as a purification measure provides a modest improvement in compatibility.
- (U) MAPO shows promise as a stabilizing plasticizer but has not been studied sufficiently to reveal possible limitations.
- (U) No crosslinking agent superior to NTEB has been found.
- (U) Catalysis of the binder crosslinking reaction may permit curing of propellant at a reduced temperature and thereby extend propellant life.
- (C) The effect of NP particle size on propellant stability is great only in unstable formulations.
- (C) A previously unreported form of instability of NP has been observed. Near 50°C, an endothermic process and evolution of gas begin. This casts further doubt on the utility of NP as a propellant ingredient.
- (C) Reta coating on NP deteriorates seriously in less than a year under mild storage conditions.
- (C) Propellants containing particulate, freshly Reta-coated NP exhibit favorable initial properties but deteriorate significantly within a few months at ambient temperature.
- (C) UTECOATING offers little promise for stabilizing NP propellants.
- (C) AP may be used in NP propellants without adverse effect on stability.
- (C) Aluminum fuel does not affect stability of NP propellants.

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UTC 2139-QTR4

SECTION III

FORMULATION STUDIES

(U) The following studies were directed toward propellant improvement by: exploiting the results of the ingredient studies discussed in section II, optimizing concentrations of ingredients, and development of techniques to minimize propellant degradation during processing.

1. CROSSLINKER CONCENTRATION

(C) The pronounced stabilizing effect of NTEB on the UTREZ/MRPX/NP system was demonstrated in the previous program⁽²⁾ and has been confirmed in the mechanistic studies at Midwest Research Institute.⁽³⁾ The ratio 1.2 equivalents NTEB:1.0 equivalents UTREZ was originally adopted to provide a minimum cure time for propellants containing Reta-coated NP. In the absence of Reta coating, much greater consumption of NTEB by aziridine-oxidizer interaction can be anticipated. Therefore, increased concentrations of NTEB can be employed without unacceptable increase in cure time.

(C) Several formulations containing increased concentrations of NTEB were prepared and tested by DTA for storage stability. Because the high concentrations of NTEB provided plasticization, the MRPX plasticizer used in previous formulations was omitted. This omission alone provided a dramatic improvement in propellant stability and provided stimulus for the plasticizer studies described in section II, 1, b. Propellants L, H, J, and K (UTX-9146, -9143, -9144, and -9145) which contain 1.2, 1.5, 2.0, and 2.5 equivalents of NTEB, respectively, required 2 weeks to cure at 60°F. Complete formulations are given in table XXVI. The DTA results shown in table XV for samples L60, H60, J60, and K60 lead to several important conclusions. First, in terms of absolute DTA values and age at occurrence of explosive combustion, these propellants are remarkably stable compared to earlier formulations with uncoated, particulate NP. Second, while stability is improved by increased NTEB concentration throughout the storage period, the greatest differences appear during the first month. Finally, when explosive combustion does occur, exotherm inception temperatures have dropped only to ca 60°C instead of the 50° to 55°C level characteristic of propellants containing MRPX plasticizer.

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TABLE XV

(U) EFFECT OF INCREASED CROSSLINKER
CONCENTRATION ON PROPELLANT STABILITY*

Sample	L 60	H 60	J 60	K 60
<u>UTX-</u>	<u>9146-1</u>	<u>9143-1</u>	<u>9144-1</u>	<u>9145-1</u>
NTEB/UTREZ equiv. ratio	1.2	1.5	2.0	2.5

DTA
Exotherm, °C/
ignition, °C
at age, days†

4	69/81	77/86	81/94	77/88
6	---	---	---	---
8	72/81	---	---	---
10	---	76/88	81/93	87/97
12	76/87	---	---	---
14	72/83	75/88	76/88	80/94
16	---	---	---	---
18	60/77	76/86	82/94	80/94
20	71/83	66/82	78/91	85/96
25	---	70/82	74/84	84/92
30	65/80	67/80	67/81	74/86
35	66/78	64/81	68/85	72/85
40	66/80	---	---	---
45	67/80	64/81	67/82	71/85
50	66/78	68/83	68/83	70/85
55	64/80	66/80	72/85	66/86
60	61/76	64/83	66/81	69/84
65	62/76	63/79	66/83	67/82
70	61/78	66/80	67/80	68/83
75	58/78X**	62/78	65/80	64/80
80	59/76X	62/78	66/80	66/78
90	62/74X	60/78	62/80	60/80
100	---	60/76X	65/81	66/82X
125	---	---	66/81	68/83
150	---	---	62/83	66/84

* - Propellants contain no MRPX. Storage at 60°F.

† - Approximate

** - X = Explosion.

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(U) In the course of a storage study, all of the samples were accidentally exposed to increased atmospheric moisture (90 ppm maximum) during a 5-day period. This exposure produced no evident trend in thermal stability but did cause surface softening of the propellant samples. Those containing the higher concentrations of NTEB (J-2.0 equivalents, K-2.5 equivalents) were much less affected and, when moisture discipline was restored, they recovered their original appearance within 3 days.

2. SOLIDS LOADING

(C) A secondary objective of the present program was to increase the ballistic performance potential of NP propellants. All of the propellants prepared in the previous program were quite underoxidized. Limited studies were conducted to increase solids loading in general and oxidizer loading in particular. Efforts to decrease binder viscosity and thereby permit processing of propellants with increased solids were discussed in section II (Ingredients Studies).

(C) Initial studies of the effects of incorporating finely divided AP and increased concentrations of atomized aluminum in the basic propellant formulation (with old Reta-coated NP) showed improved processability. Specifically, formulations UTX-8056, -8057, and -8058 mixed much more readily than did UTX-8054 (table XVI). After stability studies revealed no adverse effects resulting from use of AP and increased aluminum, formulations containing 75%w and 80%w solids were prepared (table XVII). Formulation UTX-8164 (75%w solids, 41.3%w NP, 17.7%w AP, 16%w Al) was observed to be more processable than UTX-8163 (75%w solids, 59%w NP, 16%w Al), while UTX-8165 (80%w solids, 44.8%w NP, 19.2%w AP, 16%w Al) was almost as easily handled as UTX-8163.

(C) These and other formulations containing AP and increased aluminum with old Reta-coated NP were characterized with the results shown in table XVII. No impairment of stability was observed. In fact, slight improvements were observed, but these may have merely reflected reduced concentrations of NP.

(C) Propellants containing AP and UTECOATED as well as uncoated, 30-to-40 mesh NP were prepared and studied with the results shown in tables IV and XVIII. Again, it appears that thermal stability is not importantly affected by AP. However, the tendency of the aged propellant to explode and the violence of explosion are increased in higher oxidizer loadings.

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TABLE XVI

(C) NP PROPELLANTS CONTAINING AP AND ALUMINUM

	Formulation			
	<u>UTX-8054</u>	<u>UTX-8056</u>	<u>UTX-8057</u>	<u>UTX-8058</u>
Binder, %w	35.0	35.0	35.0	35.0
NP, 4.4% Reta-coated, %w	63.0	44.1	49.0	34.3
Al, 35 μ , %w	2.0	2.0	16.0	16.0
AP, 40 μ , %w	---	18.9	---	14.7
DTA, 5°C/min				
Exotherm inception, °C	66	69	71	65
Autoignition, °C	84	87	87	88

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TABLE XVII

(C) EFFECT OF AP AND INCREASED ALUMINUM ON AGING STABILITY
OF PROPELLANTS CONTAINING RETA-COATED NP

Propellant	UTX-8141	UTX-8142	UTX-8143	UTX-8148	UTX-8149	UTX-8160	UTX-8161	UTX-8162	UTX-8163	UTX-8164	UTX-8165
Composition											
Rinder, %w	35	35	35	35	35	35	35	35	25	25	20
NP, Reta-coated, %w	63	49	49	63	49	44.1	34.3	31.5	59	41.3	44.8
Age of NP, Mo	9	9	9	10	10	10	10	10	11	11	11
AP, %w	0	0	14.7	0	0	18.9	14.7	31.5	0	17.7	19.2
Al, %w	2	16	16	2	16	2	16	2	16	16	16
Impact Sensitivity, kg cm											
1 wt	22	23	25	22	23	24	25	26	---	---	---
5 wt	24	25	21	24	25	---	21	---	---	---	---
DTA											
Exotherm, °C/ignition, °C	---	---	---	---	---	---	---	---	---	---	---
at age, weeks	2	3	6	9	12	14-1/2	18	65/81	61/86	60/84	---
Characteristics at ca 16 wk											
Gasging	Yes	No	No	Yes	Yes	Yes	No	No	---	---	---
Binder reversion	Medium	Slight	Very Slight	Severe	Severe	Medium	Slight	Very Slight	---	---	---
Unconfined combustion	Stable	Stable	Stable	Stable	Stable	Stable	Stable	Stable	---	---	---

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TABLE XVIII

(C) STABILITY OF NP/AP FORMULATIONS AT 60°F

Sample <u>UTX-</u>	<u>D</u> <u>9118-4</u>	<u>E</u> <u>9119-1</u>	<u>F</u> <u>9120-1</u>	<u>G</u> <u>9121-1</u>
Binder, * %w	35	30	25	20
Al, 35μ, %w	2	2	2	2
AP, 40μ, %w	---	20.4	21.9	23.4
NP, 30-40 mesh, %w	63	47.6	51.1	54.6

DTA Exotherm, °C/ignition,
°C, at age, days

3	67/78	67/78	70/88	67/83
5	69/80	71/82	70/79	68/81
7	64/80	67/82	64/83	66/62
11	63/80	62/83	60/81	60/78
13	66/79	62/81	64/79	63/78
17	62/77	64/79	63/79	63/78
21	61/79	64/81	63/79X [†]	64/78
26	59/77	60/77X	63/77	57/76X
31	60/75	61/76	60/72	54/76X
34	59/75	61/77	58/75X	55/76X
41	50/74X	56/79X	59/75X	56/74X
Deflagration at 32 days	1 exploded 2 normal	2 exploded	2 exploded	2 exploded violently
Deflagration at 45 days	normal	exploded	exploded violently	exploded violently

* Binder: UTREZ/NTEB, 1.0/1.2 equiv. ratio; 15% MRPX

†X = explosion

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(U) Some appreciation of the violence with which ca 2 g samples of the unconfined propellants explode can be gained by inspection of figures 1 through 4. These photographs show damage to the soft aluminum foil cups in which the test samples were ignited by use of a hot wire and a small piece of conventional AP propellant.

(C) An effort to achieve increased solids loadings without the use of AP is summarized in table XIX. An increased concentration of NTEB was used to improve stability and processability. The improved plasticizer HMN was also employed to reduce binder viscosity. Increased aluminum content as well as both available particle sizes of uncoated NP (8 to 20 mesh and 30 to 40 mesh) were used. As part of this study, the effect of binder precure was investigated. All of the propellants were far more stable than UTX-9118 (1.2 equivalent NTEB; MRPX plasticizer; 63% NP, 30 to 40 mesh 2% Al), the formulation first employed in this program. However, none could be regarded as a basis for development of a practical propellant. Binder precure, which impaired processability, offered little promise of improved stability.

3. SUMMARY OF FORMULATION STUDIES

(C) Increased concentration of the crosslinker NTEB improves the thermal stability, storage stability, and moisture resistance of propellants containing uncoated NP.

(C) Increased solids loadings without impairment of stability may be achieved by use of: increased concentration of aluminum fuel, finely divided AP, control of NP particle size, and improved plasticization of the binder.

(U) Increased O/F ratios increase the violence of explosive combustion of deteriorated propellant.

(U) Binder precure impairs processability and does not significantly improve propellant stability.

(C) No formulation has been developed which appears to offer a basis for development of a practical NP propellant.

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UTX 9118-4

DATE: 8-11-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 32 DAYS

R-70005



UTX 9118-4

DATE: 8-24-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 45 DAYS

5E66-5

Figure 1. (U) Effect of Normal Burning of UTX-9118-4,
63% Oxidizer, No AP

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UTX 9119-1

DATE: 8-24-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 45 DAYS
5866-4

UTX 9119-1

DATE: 8-11-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 32 DAYS
R-70006

Figure 2. (U) Effect of Explosive Burning of UTX-9119-1,
68% Total Oxidizer, 20% AP

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UTX 9120-1

DATE: 8-11-66

STORAGE TEMPERATURE: 50° F

TOTAL DAYS CURE: 32 DAYS

5866-3



UTX-9120-1

DATE: 8-24-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 45 DAYS

R-70007

Figure 3. (U) Effect of Explosive Burning of UTX-9120-1
73% Total Oxidizer. 22% AP

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UTX 9121-1

DATE: 8-11-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 32 DAYS

5866-2

UTX 9121-1

DATE: 8-24-66

STORAGE TEMPERATURE: 60° F

TOTAL DAYS CURE: 45 DAYS

R-70008

Figure 4. (U) Effect of Violently Explosive Burning of UTX-9121-1,
78% Total Oxidizer, 23% AP

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TABLE XIX
(U) STABILITY* OF PROPELLANTS WITH INCREASED SOLIDS LOADINGS

<u>Sample, UTX-</u>	<u>9177A</u>	<u>9177B</u>	<u>9177C</u>	<u>9177D</u>	<u>9178</u>	<u>9179</u>	<u>9180</u>	<u>9181</u>
Composition								
UTREZ (1.0 equiv.) %w	20.57	20.57	20.57	20.57	17.14	20.57	17.14	17.14
NTEB (2.0 equiv.)%w	6.43	6.43	6.43	6.43	5.36	6.43	5.36	5.36
HMN, %w	3.00	3.00	3.00	3.00	2.50	3.00	2.50	2.50
Al, 35μ, %w	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
NP, 30-40 mesh, %w	45.50	45.50	45.50	45.50	49.00	65.00	70.00	---
NP, 8-20 mesh, %w	19.50	19.50	19.50	19.50	21.00	---	---	70.00
Total solids, %w	70.00	70.00	70.00	70.00	75.00	70.00	75.00	75.00
Cure time at ambient								
temp., days	7-10	6-9	5-8	4-7	8-10	8-10	8-10	8-10
Precure, days	0	1	2	3	0	0	0	0
DTA								
Exotherm, °C/ ignition, °C <u>at age, days</u>	64/82	67/81	77/85	72/83	65/80	67/82	70/85	---
19								
23	68/80	71/81	69/81	67/81	70/79	70/82	71/79	67/80
26	64/79	67/74	64/78	81/84	66/77	66/79	67/78	68/81
30	60/76x†	64/75	67/79	63/82	60/79	63/79	60/79	68/80
34	---	---	53/77X	64/81	---	---	61/78X	65/83
Combustion after								
one month	Normal	Explosive	Explosive	---	Explosive	Explosive	Explosive	---

* - Storage at ambient temperature

† - X = Explosion.

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SECTION IV

EFFECT OF TEMPERATURE ON PROPELLANT STABILITY

(C) Under the most ideal conditions, combinations of particulate NP with useful organic fuels ignite below 100°C, following extensive exothermic reaction which begins at materially lower temperatures. For example, the most stable propellant developed under the preceding contract contained Reta-coated oxidizer and exhibited thermal behavior comparable to that of the coated oxidizer itself. Under DTA, at a heating rate of 5°C/min, exotherm inception was typically 62° to 73°C and ignition occurred at 90° to 100°C.

(U) Since the propellant was mixed, cast, and cured at ambient temperature (i.e., only ca 35°C below the exotherm temperature), it is evident that the margin of safety was slim. This operation is akin to processing an AP-based propellant at temperatures above 400°F.

(C) By use of remotely operated equipment, it might be feasible to process NP propellants at ambient temperatures. However, it is unreasonable to expect the finished propellant to survive protracted storage under this condition. It is, therefore, appropriate to consider the increase in propellant life attainable by a rather modest reduction of storage temperature.

(C) Figure 5 shows the effect of temperature on two processes; gelation of UTREZ binder containing 25% MRPX plasticizer and 1.1 equivalents of NTEB crosslinker, and the time required for visible gas formation when this binder formulation is in contact with uncoated, particulate NP. Considerable restraint must be exercised in the interpretation of these relationships. First, each curve is extrapolated on the basis of a simple process with invariant activation energy. Second, deterioration of NP propellants is known to be severe quite some time before gassing is observed. In short term studies, it has been found that the propellant may become ballistically useless before degradation is visible. Specifically, even when unconfined, the propellant may explode shortly after ignition instead of burning in an orderly manner. Finally, gel time is plotted, rather than the time required for complete cure of the binder. Earlier it was speculated that the rate of degradation of the binder by interaction with NP might decrease following cure, since mobility of incompatible species would be reduced; however, this has not proved to be the case.

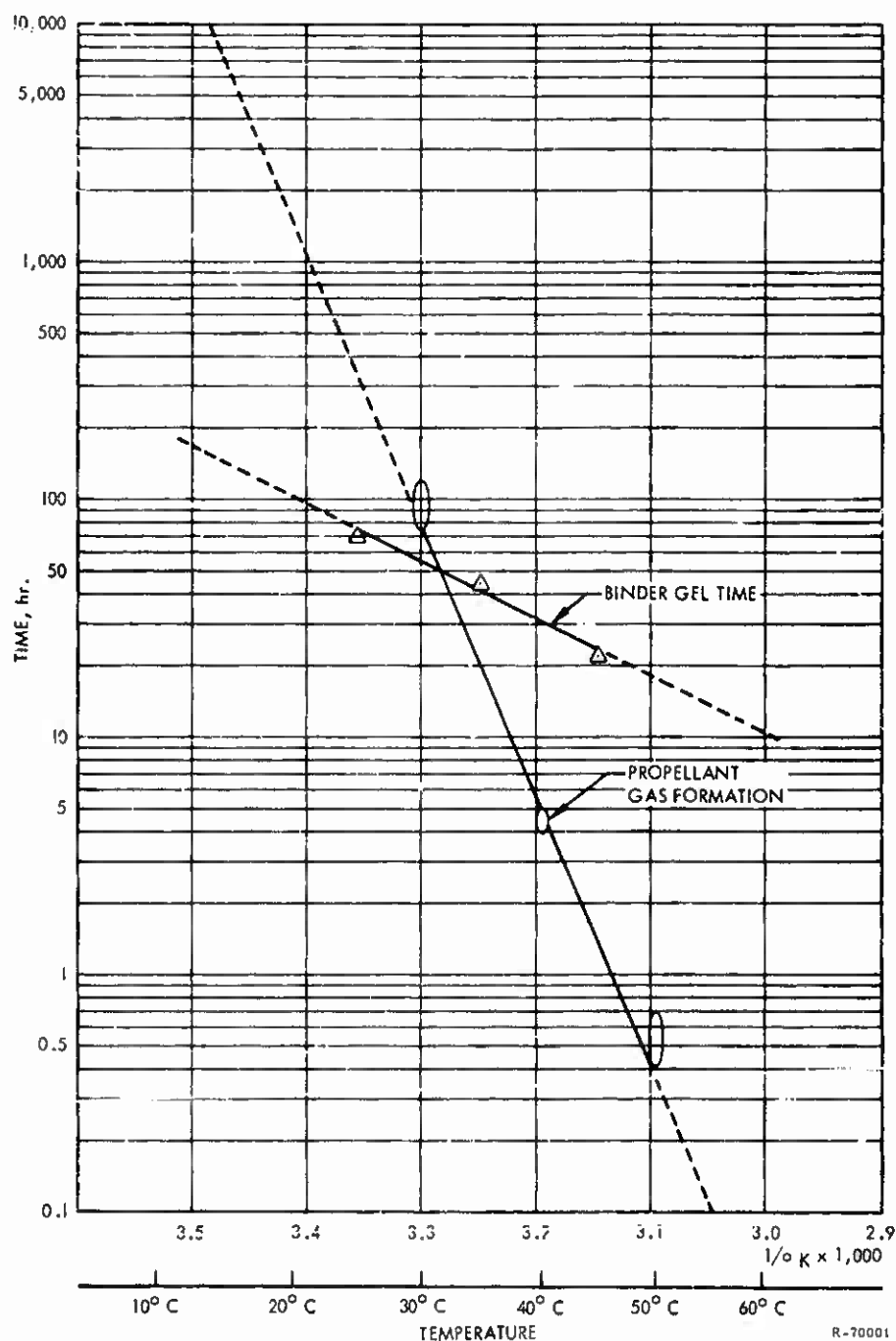
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Figure 5. (U) Effect of Temperature on Compatibility and Cure

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(U) Even with the foregoing qualifications, there was every reason to expect marked increases in propellant stability at decreased storage temperatures.

1. PROPELLANT A (UTX-9118)

(C) For initial studies, a well-characterized propellant formulation (propellant A, UTX-9118) was selected (see table XXVI). The binder formulation was optimized for use with Reta-coated NP, which interacts far less with the aziridinyl crosslinker than does the uncoated oxidizer.

(U) Samples of propellant were prepared in a dry box (moisture content less than 5 ppm) and stored at ambient or reduced temperatures within the same dry box. While samples in the individual refrigerated boxes remained at constant temperatures (60°F, 35°F, and 10°F), the samples at ambient were subject to unavoidable temperature variations. In general, ambient temperature averaged 70° to 75°F.

a. Effect of Storage at Constant Temperature on Thermal Stability

(U) One batch of propellant A (UTX-9118-1) was mixed and stored for 3 days at ambient temperature before samples were placed in storage at lower temperatures. Samples were removed periodically and subjected to DTA. Resulting data are given in table XX and are plotted in figure 6. It is evident that reduction of storage temperature greatly improved stability of the propellant.

(C) The behavior of sample A1 (ambient temperature) is representative of earlier results with propellants containing uncoated NP. The temperature of exotherm onset and ignition drops precipitously and reaches a minimum in about 1 week, then rises to or above initial levels. Interestingly, impact sensitivity of the propellant remains essentially constant (at ca 25 kg cm) throughout this period. Explosive combustion during DTA first occurs at, or shortly after, the occurrence of minimum exotherm temperature. Exotherm temperature usually provides a better indication of imminent explosive combustion than does the ignition temperature. In the case of sample A1, DTA was not performed between the 7th and 10th days. It is believed that still lower exotherms could have been observed during this period. As a rule, the exotherm temperature of this formulation decreases to at least 55°F before explosive combustion begins.

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TABLE XX
(U) THERMAL STABILITY OF PROPELLANT A (UTX-9118)

Sample	A1	A1T	A1D	A2	A2T	A2D	0	A3	A3T	A3D	B1	A4	A4T	A4D	C1
UTX-	9118-1	9118-5	9118-6	9118-1	9118-5	9118-6	9118-4	9118-1	9118-5	9118-6	9118-2	9118-1	9118-5	9118-6	9118-5
Storage history, days/Temp.	-/ambient	-/ambient	-/ambient	5/ambient	7/ambient	23/ambient	-60° F	5/ambient	7/ambient	10/ambient	5/ambient	5/ambient	7/ambient	20/ambient	-/10° F
DTA															
Exotherm, °C/															
ignition, °C/															
at end, days															
5	6/85	---	---	---	---	---	57/78	---	---	---	---	---	---	---	75/81
5	67/77	66/78	66/82	61/76	---	---	66/80	55/31	---	---	66/60	62/78	---	---	65/77
7	58/75	---	64/77	61/77	---	---	66/60	65/77	---	---	62/77	59/77	---	---	66/77
9	64/81X	60/75	59/76	---	---	---	---	---	---	---	---	---	---	---	---
11	---	59/76	---	58/78	56/75	---	65/80	62/76	---	---	62/76	62/78	---	---	67/78
13	65/84X	56/75	52/74X	62/78	---	---	64/79	61/75	---	---	---	61/76	---	---	65/78
15	68/85	57/75	62/73	---	52/76	---	---	---	59/78	---	---	---	57/77	---	---
17	65/87	52/75	48/72	---	51/77	56/71	62/77	---	---	---	---	---	---	57/72	---
20	---	---	57/77X	64/77	---	60/76	61/79	62/78	61/75	62/76	60/79	58/78	55/76	---	62/80
25	75/82X	---	64/76	56/75	52/76X	58/74	59/77	59/76	56/78	---	52/77	51/75	58/75	57/74	---
30	72/84X	---	---	59/75X	53/73X	57/74	60/75	56/76	61/77	60/76	65/76	60/75	57/77	57/72	59/78
55	---	---	---	51/74X	---	60/72	59/75	---	59/79	66/78	---	---	56/75	---	---
40	---	---	---	55/75X	---	58/72	50/74X	58/76	58/76	60/76	55/76	51/74X	57/78	62/76	---
45	---	---	---	---	---	56/75	---	---	60/79	62/76	---	---	51/77	55/70	60/77
60	---	---	---	---	---	60/78	---	61/75	62/75	60/76	---	---	51/75	59/72	---
70	---	---	---	---	---	---	---	55/75	60/72	52/72	56/77	50/75	51/75	---	---
80	---	---	---	---	---	---	---	---	56/75	59/75	61/77	---	---	57/72	66/75X
100	---	---	---	---	---	---	---	55/75	57/74	61/75	56/75	52/76	58/75	58/75	55/74
125	---	---	---	---	---	---	---	55/74X	56/70	58/73	56/75	---	56/72X	59/75	57/76
150	---	---	---	---	---	---	---	60/74	60/75	---	57/71	---	56/70	---	64/74
200	---	---	---	---	---	---	---	---	56/75	---	---	---	60/75	---	---
250	---	---	---	---	---	---	---	---	55/71	---	---	---	58/71	---	---
300	---	---	---	---	---	---	---	---	60/74	---	56/70	---	56/70	---	---

* ambient temperature below normal during this period.

† approximate

** X = explosion

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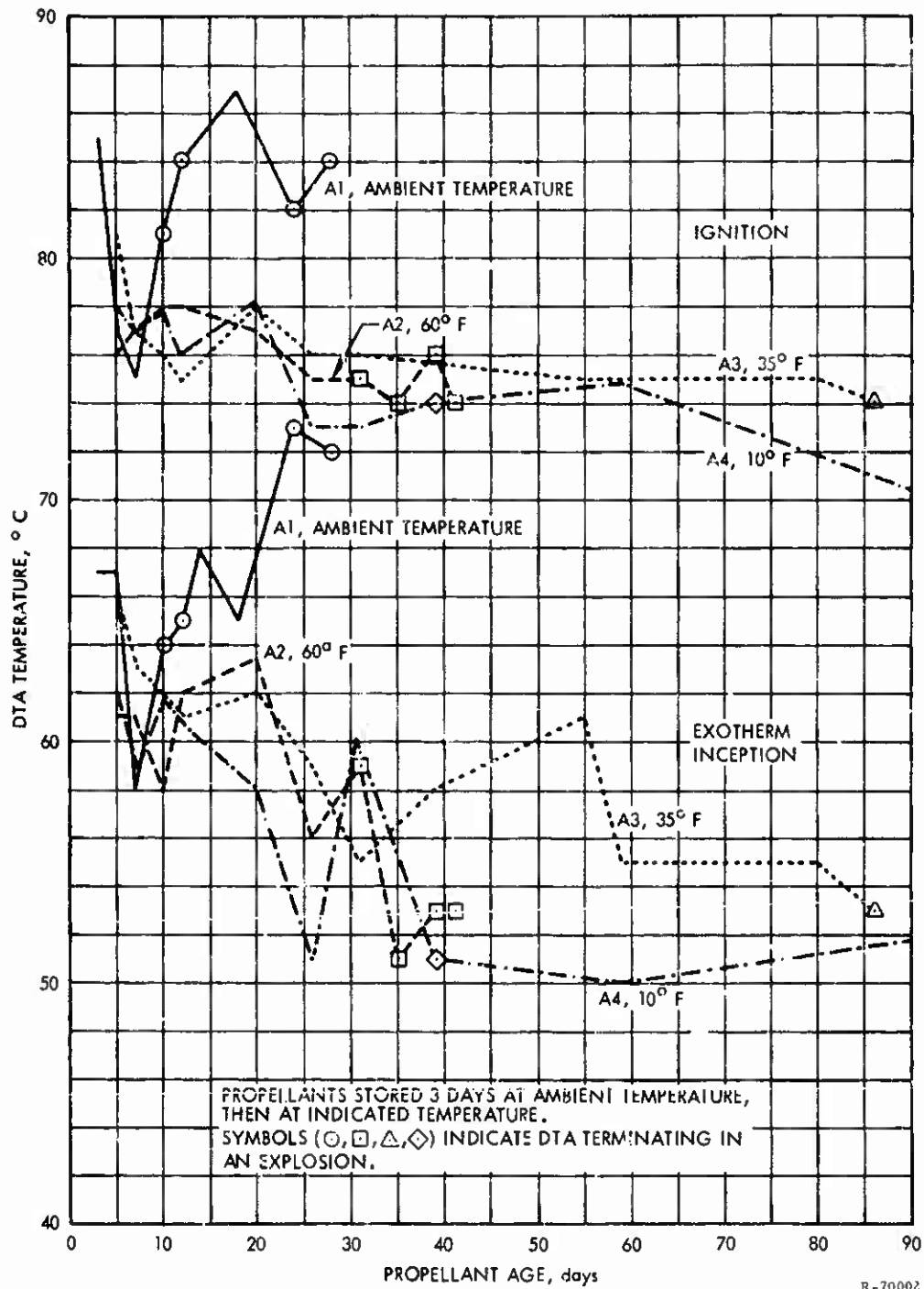


Figure 6. (U) Storage Stability of Propellant A (UTX-9118-1) at Constant Temperature

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(U) Samples A1T and A1D were placed in storage during a period of reduced ambient temperature. This accounts for their reduced rate of degradation relative to sample A1. The same consideration applies in comparing A2T and A2D with A2, A3T and A3D with A3, and A4T and A4D with A4. Note, however, that samples of the 2, 3, and 4 series were stored at ambient temperature for differing periods in order to cure the propellants prior to storage at reduced temperatures. In general, samples D and C1, which were placed in storage at reduced temperatures immediately after mixing, deteriorated much more slowly than corresponding samples which had been cured at ambient temperature.

(U) Using age at the first occurrence of explosive combustion as a crude standard for samples A1, A2, A3, and A4, the effect of storage temperature is: ambient, 10 days; 60°F, 31 days; 35°F, 86 days; and 10°F, 39 days.

(U) Comparable studies with subsequent batches of propellant A (control samples for tensile specimens and deflagration tests: A1T, A2T, A3T, A4T, A1D, A2D, A3D, and A4D) revealed a similar pattern of response to storage temperature. However, these samples were cured at lower ambient temperatures prior to storage and therefore generally exhibited greater stability. Sample A3T, for example, survived 10 months at 35°F without evident degradation or exploding during DTA.

(C) Decreased stability at 10°F compared to 35°F is unexpected but real. While the mechanisms responsible for this behavior are not obvious, another phenomenon peculiar to samples stored at 10°F is probably related. Over a period of weeks, a white, cloudy material condenses on the internal surfaces of the glass beakers containing these samples. While the amount of condensate is too small to characterize, it resembles NP, in that it "smokes" when exposed to humid air, is a powerful oxidizing agent, and is strongly acidic when dissolved in water. It is striking that no such condensate appears when formulations containing increased concentrations of the basic crosslinker NTEB are similarly stored. It appears probable that the condensate is NP which has "volatilized" by the mechanism proposed by investigators at Midwest Research Institute.⁽³⁾

(C) Another unexpected effect of low temperature storage deserves comment. A sample (C3) of freshly prepared propellant stored for 3 days at 10°F and 9 days at 35°F was

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transferred to storage at 60°F. Within 1 week, this sample cured well and showed good thermal stability without explosive combustion until the 52nd day after mixing. In contrast, when initial storage consisted of 3 days at 10°F and 29 days at 35°F and was followed by storage at ambient temperature, the sample (C4) failed to cure. Therefore, it appears that at 35°F a stabilizing process accompanied by crosslinker depletion occurs. This process may be NP-catalyzed homopolymerization of NTEB.

b. Effect of Prior Storage at Low Temperatures
on Thermal Stability

(C) To explore the possibility of exploiting low temperature exposure to stabilize NP propellants, a number of storage tests were conducted without altering the propellant formulation. Results of DTA are shown in table XXI.

(U) Figure 7 indicates that 9 days of storage at 35°F failed to improve stability during subsequent storage at 10°F. It is evident, however, that the propellant used in this series was inferior to the particular batch employed in the test shown in figure 6.

(U) Figure 8 shows test results with the same formulation which was placed in storage at 10°F immediately after mixing. Therefore, these samples were spared the initial thermal exposure suffered by the propellants previously discussed. After 3 days at 10°F, a portion of the propellant was placed in storage at 35°F; subsequently, samples were removed from 35°F storage and were placed in storage at 60°F and at ambient temperature.

(U) Comparing the results of this test series with those shown in figure 6, it can be seen that early storage at low temperature promotes stability. First, the sample (C1) stored continuously at 10°F remained quite stable until sometime between the 41st and 69th days. The sample (C2) at 35°F remained stable for the duration of the test (ca 125 days). The sample (C3) at 60°F did not exhibit explosive combustion until the 52nd day. Of course, these improvements in stability might be explained simply by the minimization of initial exposure to ambient temperature. However, the behavior of the sample at ambient temperature (C5) seems to show a beneficial effect of 32 days storage at reduced temperatures (3 days at 10°F and 29 days at 35°F). Following this storage, sample C5 survived at ambient temperature of 9 days with good thermal stability and did not explode

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TABLE XXI

(U) EFFECT OF PRIOR LOW TEMPERATURE STORAGE ON THERMAL STABILITY
OF PROPELLANT A (UTX-9118)

Sample	B1	B2	C1	C2	C3	C4	C5
UTX-	9118-2	9118-2	9118-3	9118-3	9118-3	9118-3	9118-3
Storage history, days/temp.	3/ambient -/-35°F	3/ambient 9/35°F -/-10°F	-/-10°F - -	3/10°F -/-35°F	3/10°F 9/35°F -/-60°F	3/10°F 29/35°F -/-ambient (-/-valued (-/-stainer)	3/10°F 29/35°F -/-ambient
DTA Exotherm, °C/ ignition, °C at age, days ^{a)}	3 5 7 9 11 13 15 17 20 25 30 35 40 45 50 60 70 80 100 125 150 200 250 300	--- 60/80 62/77 --- 62/76 --- --- --- 60/79 52/77 63/76 --- 55/76 --- 54/77 61/77 56/73 54/73 57/71 --- --- --- 56/70	--- --- --- --- --- --- --- --- 61/80 51/75X 49/75 --- 48/71 --- 56/76 --- --- --- --- --- --- --- --- --- --- ---	--- 75/81 63/77 66/77 --- 67/78 63/78 --- --- 62/80 --- 59/78 --- --- 60/77 --- 46/75X 55/74 57/76 64/74 --- --- --- --- ---	--- 62/78 64/85 --- 66/79 66/81 70/87 68/82 --- 73/82 68/81 --- 66/80 --- --- 66/81 60/78 60/74 64/78 --- --- --- --- ---	--- --- --- --- --- 70/84 65/79 --- 64/79 62/77 --- 54/76 --- 54/76X --- 64/77 56/75 70/83X 64/81 --- --- --- --- ---	--- --- --- --- --- --- --- --- --- --- 63/78 61/75 50/76X 65/81X --- --- --- --- --- --- --- --- --- --- ---

a) approximate

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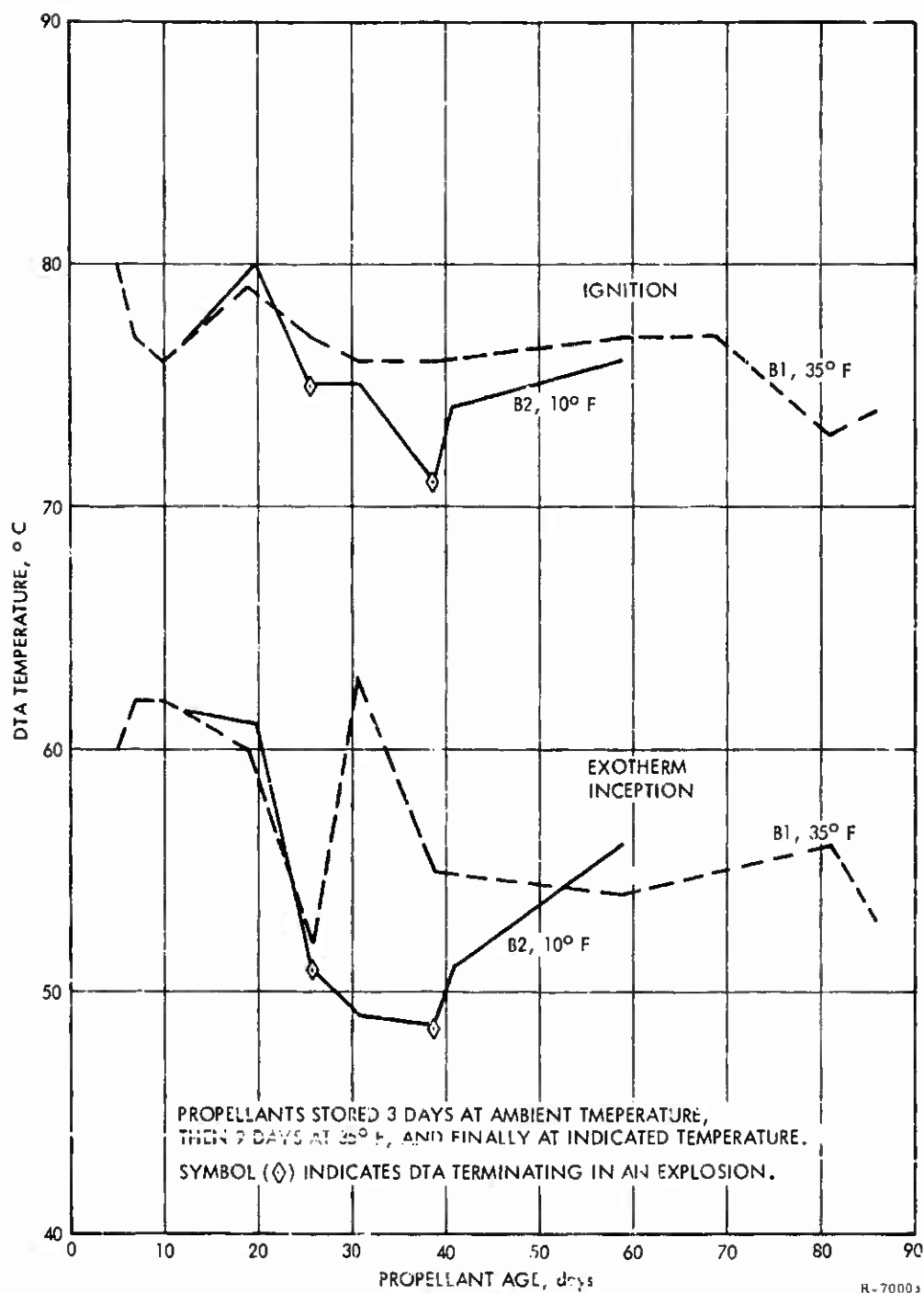


Figure 7. (U) Effect of Prior Storage at 35°F on Stability of Propellant A (UTX-9118-2) at 10°F

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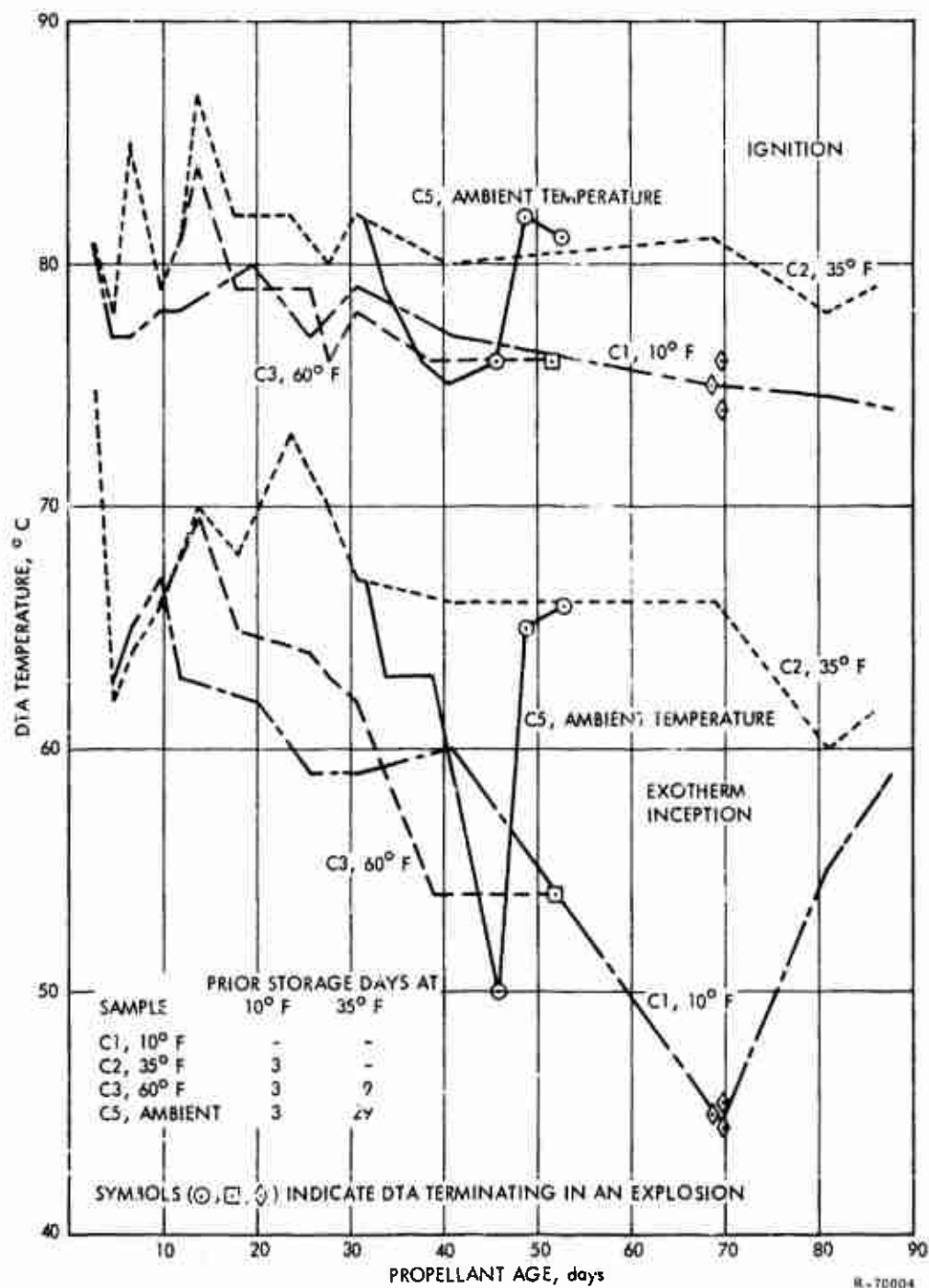


Figure 8. (U) Effect of Prior Storage at Low Temperatures on Stability of Propellant A (UTX-9118-3) at Elevated Temperatures

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until the 14th day. By comparison, sample A1, which was exposed to ambient temperature continuously after mixing, was stable for 7 days and exploded when tested on the 10th day. It is clear that the difference between A1 and C5 is not great, but it still must be recognized that the latter was 32 days old when ambient storage began.

c. Deflagration and Explosive Combustion

(C) While poor storage stability and low ignition temperature of NP propellants are well recognized, there is limited appreciation of their potentially dangerous combustion characteristics. Many attempted motor firings of NP propellants have resulted in what is euphemistically termed "over-pressurization." When similar explosions occur without benefit of a confining motor case, a different term, such as explosive combustion, seems appropriate. This phenomenon has been observed many times during UTC's studies of NP propellants and is not yet understood in detail. However, certain general factors are known which appear equally applicable to the results reported by other investigators.

(C) In most cases the temperature of the propellant under test is usually only a little (50° to 80°C) below the ignition temperature. In addition, deterioration leading to gas formation, hence porosity, is in progress. Resultant debonding of binder from the oxidizer may provide paths for extremely rapid propagation of the ignition front. Finally, it appears likely that the interaction of NP with organic substrates would produce explosive such as organic nitrates and perchlorates as well as free perchloric acid.

(C) It appears significant that in studies at UTC, explosive combustion of unconfined propellant has not occurred with freshly prepared formulations or with any propellant, however deteriorated, in which all of the NP is Reta-coated. It should not be assumed, however, that stable combustion at atmospheric pressure implies that combustion will be stable at higher pressures. Results of micromotor tests conducted in the previous program⁽²⁾ suggest that propellant degradation may first be detected by occurrence of abnormal combustion at some threshold pressure.

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(U) One-g, cylindrical samples of propellant A were burned without confinement after storage in the dry box at ambient temperature at 60°F. The results of these tests are shown in table XXII. Apparently the occurrence of explosive combustion cannot be predicted accurately on the basis of age or DTA of the sample. However, DTA can serve as a rough guide. In the case of propellant A, explosive combustion can be expected after the exotherm inception temperature under DTA has dropped to ca 55°C. Frequently, this temperature begins to increase shortly before explosive combustion is observed. In this study, propellant stored at 60°F survives about three times as long as that stored at ambient temperature. This is consistent with the results of DTA discussed previously.

d. Mechanical Properties and Impact Sensitivity

(U) A limited study of the mechanical properties of propellant A was undertaken. Microtensile specimens were prepared, and tests were conducted as indicated in table XXIII. Results of a parallel study of the thermal stability of this batch of propellant are shown in table XX (A1T, A2T, A3T).

(U) The tensile properties of propellant A compare unfavorably with those of a comparable propellant formulated with Reta-coated oxidizer (σm, 36 psi; εm, 43%). This is attributed to depletion of NTEB by interaction with the uncoated NP in propellant A.

(U) The impact sensitivity of propellant A after curing 7 days at ambient temperature was found to be 31 kg cm (2 kg weight). This value is typical for propellant A regardless of age, providing the sample has not been exposed to moisture.

2. PROPELLANT B (UTX-9171)

(C) The second extensive study of the effect of storage temperature on propellant stability was conducted with an intrinsically more stable formulation, UTX-9171 (propellant B). This formulation, which contained 35%w binder with no plasticizer, 63%w uncoated 8-to-20 mesh NP, and 2%w aluminum, required 11 days to cure at ambient temperature.

a. Effect of Storage Temperature on Thermal Stability

(U) Table XXIV shows the DTA results of samples stored under the conditions previously described.

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TABLE XXII

(U) COMBUSTION OF PROPELLANT A (UTX-9118-6)

<u>Sample</u>	<u>Storage History</u> <u>Days - Temperature</u>	<u>Combustion Tests</u> <u>Number - Result</u>	<u>DTA</u> <u>Exotherm/Ignition</u> <u>°C</u>
A1D	13 - ambient	1 - normal	52/74 exploded
A1D	17 - ambient	[1 - normal 2 - exploded]	48/72
A1D	20 - ambient	3 - normal	58/76 exploded
A1D	23 - ambient	3 - normal	62/76
A2D	[10 - ambient 14 - 60°F]	1 - normal	62/75
A2D	[10 - ambient 24 - 60°F]	3 - normal	60/72
A2D	[10 - ambient 31 - 60°F]	2 - normal	57/72
A2D	[10 - ambient 35 - 60°F]	2 - normal	56/75
A2D	[10 - ambient 38 - 60°F]	2 - exploded	60/78

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TABLE XXIII

(U) TENSILE PROPERTIES OF PROPELLANT A (UTX-9118-5)

<u>Storage Condition</u>	<u>σ_m psi</u>	<u>ϵ_m %</u>
8 days ambient temperatura	7.4	25.9
8 days ambient temperature	9.3	29.0
10 days ambient temperatura	5.1	16.0
10 days ambient temperature	9.1	28.7
13 days ambient temperatura	Too weak to test	
7 days ambient, 8 days 60°F	7.4	20.4
7 days ambient, 8 days 60°F	9.3	26.6
7 days ambient, 10 days 60°F	9.8	17.8
7 days ambient, 10 days 60°F	11.0	30.5
7 days ambient, 17 days 35°F	10.2	21.8

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TABLE XXIV

(U) EFFECT OF STORAGE TEMPERATURE
ON THERMAL STABILITY OF PROPELLANT B (UTX-9171)

Sample, UTX-	9171-2	9171-3	9171-2	9171-3	9171-2	9171-2
Storage, days/ temperature	-/ ambient	-/ ambient	12/ ambient -60°F	-60°F	12/ ambient -35°F	12/ ambient -10°F
DTA						
Exotherm, °C/ ignition, °C at age, days*						
4	74/88	---	---	76/92	---	---
6	---	81/98	---	74/92	---	---
8	78/87	85/99	---	74/90	---	---
10	---	---	---	---	---	---
12	69/84	---	---	74/90	---	---
14	71/87	78/91	---	---	---	---
16	---	78/92	---	73/89	---	---
18	---	---	---	74/89	---	---
20	75/92	77/94	76/92	71/88	77/92	76/90
25	---	71/87	76/89	72/89	77/90	77/91
30	74/89	75/92	78/90	73/88	76/90	73/88
35	---	74/90	---	72/90	---	---
40	73/87	70/89	76/91	69/87	75/91	71/88
45	72/88	69/85	73/87	68/85	76/92	72/86
50	72/88	63/86	70/89	---	70/88	71/88
60	70/89	68/86X†	70/86	---	71/86	70/88
70	68/86	---	70/86	---	72/88	70/87
80	68/88	---	68/86	---	70/88	67/86
100	68/85	---	69/86	---	72/87	69/86
125	69/84	---	68/83	---	72/88	71/84
150	71/87	---	72/83	---	71/82	73/84
175	77/88	---	74/87	---	73/84	74/84
200	78/90	---	---	---	---	---

* - Approximate

† - X = Explosion

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(U) The pattern of behavior in this study differs markedly from that of propellant A. The effect of storage temperature was much less than that observed with propellant A, and after 2 months all differences had essentially disappeared.

(U) Several results of this study are disturbing. First, in the single instance that explosive combustion occurred during DTA (UTX-9171-3, ambient temperature, 60 days) the exotherm inception temperature had dropped to only 68°C in contrast to the 55°C level usually observed with propellant A. While other samples of propellant B exhibited similarly low exotherms, they did not explode. Furthermore, in none of the deflagration experiments subsequently described did unconfined samples of propellant B burn abnormally. Therefore, the state of degradation of all of the stored samples remains somewhat in doubt.

(C) A second observation may be particularly important. After 150 days, the sample of UTX-9171-2 stored at ambient temperature was placed in a sealed container to prevent contamination during a routine cleanup. When the container was opened, the sample was observed to have softened appreciably. However, after continued exposure to the dry box atmosphere the sample rehardened, and thereafter its thermal stability increased. This behavior is typical of deteriorated NP propellant. Although ambient temperature was above normal during this period, the confinement is believed to be a key factor in the softening process. There is reason to suspect that all of the storage tests in this program were artificially mild in that the atmosphere of the dry box was continuously recirculated through a caustic bed. Therefore, any volatile acidic materials evolved by the stored samples would have been trapped and thereby prevented from interacting with the samples.

(U) It may be significant (and ominous) that all of the samples stored for 6 months exhibited slightly increased thermal stability after about 3 months.

b. Deflagration

(U) Experiments identical to those reported for propellant A resulted in normal combustion regardless of sample age (up to 20 weeks) and storage temperature (maximum, ambient).

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c. Mechanical Properties

(U) The tensile properties of stored specimens of propellant B are shown in table XXV. Although these properties are not impressive by ordinary propellant standards, they represent a great improvement over those of crosslinker-deficient propellant A. Storage at ambient temperature results in decreased strain capability without a corresponding increase in tensile strength. Similar deterioration appears to occur at 60°F. The samples at 35° and 10°F had not similarly deteriorated at the time of testing.

3. SUMMARY OF EFFECT OF TEMPERATURE ON PROPELLANT STABILITY

(C) Storage at reduced temperatures (65°, 35°, and 10°F) reduces the rate of deterioration of propellants containing uncoated NP. This expected effect is more pronounced with a formulation deficient in the stabilizing crosslinker NTEB.

(C) In the case of such a formulation, storage at 35°F affords greater stability than storage at 10°F. This unexpected result may be related to retention at 10°F of migrating NP which is "volatilized" and thereby lost from samples stored at higher temperatures.

(U) Evidence has been obtained that a stabilizing process with concomitant depletion of crosslinker occurs at reduced temperature.

(U) A sample of the less stable propellant survived 10 months at 35°F without exhibiting explosive combustion or visible degradation. Samples of the more stable propellant stored at 35° and 10°F underwent little change during a 6-month period.

(U) There is reason to suspect that propellant degradation would have been more severe if samples had been stored in sealed containers or had been of such size that escape of volatile products had been reduced significantly.

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TABLE XXV

(U) TENSILE PROPERTIES OF PROPELLANT B
(UTX-9171)

<u>Sample, UTX-</u>	<u>Age,* days</u>	<u>Storage Temperature</u>	<u>σ m, av.</u>	<u>ϵ m, av.</u>
9171-2	13	Ambient	26.2	34.1
9171-2	21	Ambient	47.7	21.9
9171-3	34	Ambient	45.1	14.7
9171-3	41	Ambient	46.6	13.1
9171-3	42	60°F	47.2	21.4
9171-3	49	60°F	50.2	15.8
9171-2	70	35°F	46.7	24.7
9171-2	77	10°F	32.8	36.4

* Includes 12-day cure at ambient temperature.

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UTC 2139-QTR4

SECTION V

MECHANISM OF NP PROPELLANT DEGRADATION

(C) The final report⁽³⁾ of the Midwest Research Institute studies of NP provides what is believed to be the most complete and useful mechanistic treatment of the problems of exploiting this oxidizer. These studies demonstrated conclusively the intolerable reactivity of NP not only with the binder ingredients employed in the present program at UTC but also with specially purified model compounds. Furthermore, the intrinsic instability of the best available NP was demonstrated.

(C) Results of the present investigation are completely consistent with those of the mechanistic study and do not materially alter the gloomy picture. However, work at UTC under the previous and present programs provides additional insight concerning processes which have prevented practical use of NP.

(C) An important property of NP which apparently has not been observed previously deserves special comment. This is the occurrence of an endothermic process at about 50°C accompanied by gas evolution. All previous studies of the thermal decomposition of NP have indicated a useful upper temperature limit approaching 70°C. Had the lower temperature instability been known, it is doubtful that NP would have received as much emphasis as it has.

(C) A second noteworthy process is the apparent migration of NP via the vapor phase from propellants stored at 10°F. This, coupled with the probability that NP can pass through the best available encapsulating material, Reta coating⁽³⁾ poses a very serious problem.

(C) The detailed mechanisms of propellant deterioration and explosive combustion of deteriorated propellant are still not known. However, on the basis of time of occurrence or color changes of the propellant it appears likely that they are intimately related to the generation and sudden disappearance of nitric acid observed at Midwest Research Institute and to explosions of confined samples of Reta-coated oxidizer at Union Carbide Corp.⁽¹⁾

(C) The only obvious means of imparting significant stability to an NP propellant is to employ basic substances capable of scavenging acidic materials, including the nitronium ion, NO_2^+ . In the present investigation, NTEB served this function.

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(C) Prior to undertaking contractual work on NP and several years before Olah's publication⁽⁵⁾ on the subject, UTC prepared and characterized remarkably stable products of the reaction of NP with pyridine and with oxidation-resistant pyridine derivatives. Use of this reaction to stabilize NP propellants is the subject of pending patent.* Because pyridine and its appropriate derivatives are very weak bases, they do not compete effectively with NTEB in the propellants studied in the present program.

(C) Due to "volatilization" of NP, it appears that achievement of acceptable propellant stability would require sufficient base to convert all of the NP to stable products. This, of course, would render the propellant far less energetic than state-of-the-art AP systems.

* Presently under Secrecy Order with Permit A of the United States Patent Office.

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UTC 2139-QTR4

SECTION VI

SUMMARY AND CONCLUSIONS

(C) Work under the present contract has resulted in the development of improved propellant formulations containing particulate NP and UTREZ prepolymer. Thermal and storage stability of formulations containing uncoated NP have been increased by development of superior plasticizers and optimization of the concentration of a stabilizing crosslinker. Other ingredients and techniques which have been tested offer the possibility of further, but limited, improvements in stability. Increased theoretical ballistic performance has been achieved through increased solids loadings attained by control of NP particle size, use of finely divided AP as a supplementary oxidizer, and incorporation of increased amounts of aluminum fuel.

(C) The effect of thermal exposure on propellant stability has been studied in detail, and propellant life has been extended considerably by reduction of storage temperature. This study has also provided new insight concerning the processes which cause degradation of NP propellants.

(C) Judging from experience with NP at UTC, as well as results of investigations conducted elsewhere, it appears unlikely that NP can be employed to produce practical propellants. The following considerations constitute the basis for this pessimistic judgement.

- A. (U) Maintenance of adequate moisture discipline throughout processing and storage is feasible in the laboratory but would be prohibitively expensive for a manufacturing facility.
- B. (C) The ingredient purification procedures required for even marginal stability of NP propellants are also extremely expensive.
- C. (U) The hazard of mixing large quantities of propellant within 50°C of the temperature of exotherm leading to ignition is unreasonable.
- D. (C) It is still not possible to formulate castable compositions containing NP that offer ballistic performance superior to safe, state-of-the-art propellants.

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- E. (C) All NP propellants deteriorate rather rapidly, even under mild storage conditions.
- F. (C) Deterioration of NP propellants leads not merely to ballistic unreliability but to the hazard of explosion.
- G. (U) There is reason to believe that the rate of deterioration increases with the mass of propellant and with confinement.
- H. (C) Increased intrinsic stability of NP would be required to justify further efforts to employ this oxidizer in a practical rocket propulsion system.

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UTC 2139-QTR4

TABLE XXVI
(c) PROPELLANT FORMULATIONS

Propellant	Binder ^{a)}				Solids				AP, 40, %w	Al, 3% %w
	%w	MTES equiv.	Plasticizer Type	%w ^{b)}	%w	RP, 30-60 mesh, %w	RP, 8-20 mesh, %w	Coating %w ^{c)}		
1 A	40	2.0	MAPO	5	60	60	---	---	---	---
5	40	2.0	MAPO	5	60	---	60 ^{d)}	---	---	---
11 A	40	2.0	MAPO	3	60	---	---	---	---	---
B	40	2.5	MAPO	3	60	---	60	---	---	---
C	40	2.5	MAPO	5	60	---	60 ^{d)}	---	---	---
10-1	35	2.0	---	---	65	---	45	---	---	---
-2	35	2.0	---	---	65	65	---	---	---	---
-3	55	2.0	---	---	65	---	63	---	---	2
-4	35	2.0	---	---	65	65	---	---	---	2
-5	35	2.5	---	---	65	---	65	---	---	---
-6	35	2.5	---	---	65	65	---	---	---	---
-7	35	2.5	---	---	63	---	63	---	---	2
-8	35	2.5	---	---	65	63	---	---	---	2
210-125-1	35	2.0	HNH	10	65	---	65	---	---	4
-2	35	2.0	HNH	5	65	---	65	---	---	---
-3	55	2.0	MAPO	10	65	---	65	---	---	2
-4	35	1.3	HNH	10	65	---	63	---	---	2
170-700	41	1.2	HRFX	13	39	56	---	Rate, 3.3	---	3
-8054	35	1.2	HRFX	15	65	63	---	Rate, 4.4	---	2
-8055	35	1.2	HRFX	15	65	65	---	Rate, 4.4	---	2
-8056	35	1.2	HRFX	15	63	64	---	Rate, 4.4	19	2
-8057	35	1.2	HRFX	15	63	69	---	Rate, 4.6	---	16
-8058	35	1.2	HRFX	13	63	36	---	Rate, 4.6	15	16
-8171	35	1.2	HRFX	15	65	65	---	Rate, 4.6	---	2
-8172	35	1.2	HRFX	13	65	49	---	Rate, 4.6	---	16
-8173	35	1.2	HRFX	13	63	34	---	Rate, 4.6	13	16
-8174	35	1.2	HRFX	15	65	63	---	Rate, 4.4	---	2
-8175	35	1.2	HRFX	15	65	49	---	Rate, 4.6	---	16
-8176	35	1.2	HRFX	13	65	44	---	Rate, 4.4	19	2
-8177	35	1.2	HRFX	15	63	34	---	Rate, 4.4	15	16
-8178	35	1.2	HRFX	15	65	32	---	Rate, 4.4	31	2
-8179	23	1.2	HRFX	15	75	59	---	Rate, 4.4	---	16
-8180	25	1.2	---	15	75	41	---	Rate, 4.4	18	16
-8181	20	1.2	---	15	80	45	---	Rate, 4.4	19	16
-8182	25	---	UPE	15	75	59	---	UTECONAT-M, 0.8	---	16
-8183	25	---	Squalene	15	73	39	---	UTECONAT-M, 0.8	---	16
-8184	25	1.2	HRFX	15	75	41	---	UTECONAT-M, 0.8	16	16
-8185	25	1.2	Squalene	15	75	41	---	UTECONAT-M, 0.8	18	16
-8186	25	1.2	HRFX	15	75	39	---	UTECONAT-M, 0.8	---	16
-8187	25	1.2	HRFX	15	75	39	---	Rate, 4.4	---	16
-8188	25	1.2	HRFX	15	73	59	---	UTECONAT-M, 0.8	---	16
-8189	35	1.2	HRFX	15	63	63	---	---	---	2
-8190	30	1.2	HRFX	15	70	48	---	---	20	2
-8191	25	1.2	HRFX	13	75	51	---	---	22	2
-8192	20	1.2	HRFX	15	60	53	---	---	23	2
-8193	35	1.5	---	---	65	65	---	---	---	---
-8194	35	2.0	---	---	65	65	---	---	---	---
-8195	35	2.3	---	---	65	45	---	---	---	---
-8196	35	1.2	---	---	65	61	---	---	---	---
-8197	33	1.2	HRFX	13	65	---	63	---	---	2
-8198	33	2.0	---	---	63	63	---	---	---	2
-8199	35	2.0	---	---	65	---	63	---	---	2
-8200	35	2.0	---	---	63	---	63	---	---	2
-8201	30	2.0	HNH	10	70	46	19	---	---	5
-8202	25	2.0	HNH	10	73	49	21	---	---	5
-8203	30	2.0	HNH	10	70	63	---	---	---	3
-8204	25	2.0	HNH	10	73	70	---	---	---	5
-8205	23	2.0	HNH	10	73	70	---	---	---	3
-10000	30	2.0	---	---	70	---	66	Rate, 7.8	---	2
-10001	32	2.0	---	---	68	---	66	Rate, 4.3	---	2
-10002	33	2.0	---	---	67	65	---	Rate, 3.6	---	2
-10003	29	2.0	---	---	71	69	---	Rate, 8.4	---	2

a) UTECONAT = 1.0 equiv. in all formulations
b) %w of binder
c) %w of RP
d) Particle size reduced by crushing

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UTC 2139-QTR4

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APPENDIX**FACILITIES**

(U) During the previous program, ingredients were prepared and purified in ordinary laboratory equipment; therefore, batch sizes were limited to the fractional-pound level. To provide sufficient supplies of ingredients for the present program, scaled-up equipment was constructed. In addition, a surveillance facility was constructed to permit storage of propellant at various temperatures in a dry atmosphere.

1. OXIDIZER TREATMENT

(C) Figure 9 shows the equipment employed to dry NP and other solid ingredients under vacuum. The process for drying NP is as follows.

(C) The oxidizer is transferred in a dry box to the heavy-walled Erlenmeyer flask visible at the lower left of figure 9. A closure consisting of an industrial joint, a stopcock, and a tapered glass joint is attached to the flask and sealed by a Teflon O-ring and clamp. The closed assembly is attached to the vacuum line and the entire system is evacuated by a mechanical pump until the pressure is reduced to 2×10^{-2} torr. At this pressure, the oil diffusion pump is started and the pressure is further reduced to ca 10^{-5} torr. Three traps cooled with liquid nitrogen prevent volatile materials from entering the pumps. Customarily, 100-g lots of NP are dried for at least 16 hours at ambient temperature. At the end of the drying period the stopcock on the Erlenmeyer flask closure is closed so that no gas is admitted to the flask when the rest of the system is returned to atmospheric pressure. The still-evacuated flask is returned to the dry box before being opened.

2. UTREZ AND PLASTICIZER TREATMENT

(U) Details of the methods of purifying UTREZ and MRPX plasticizer were given in the final report covering the previous program.⁽²⁾ The sequence of treatments for UTREZ are hypobromite oxidation, nitric acid oxidation, extraction with silica gel, and vacuum stripping. For MRPX, the sequence involves extraction with concentrated sulfuric acid, nitric acid oxidation, extraction with silica gel, vacuum distillation, and final drying over phosphorous pentoxide.

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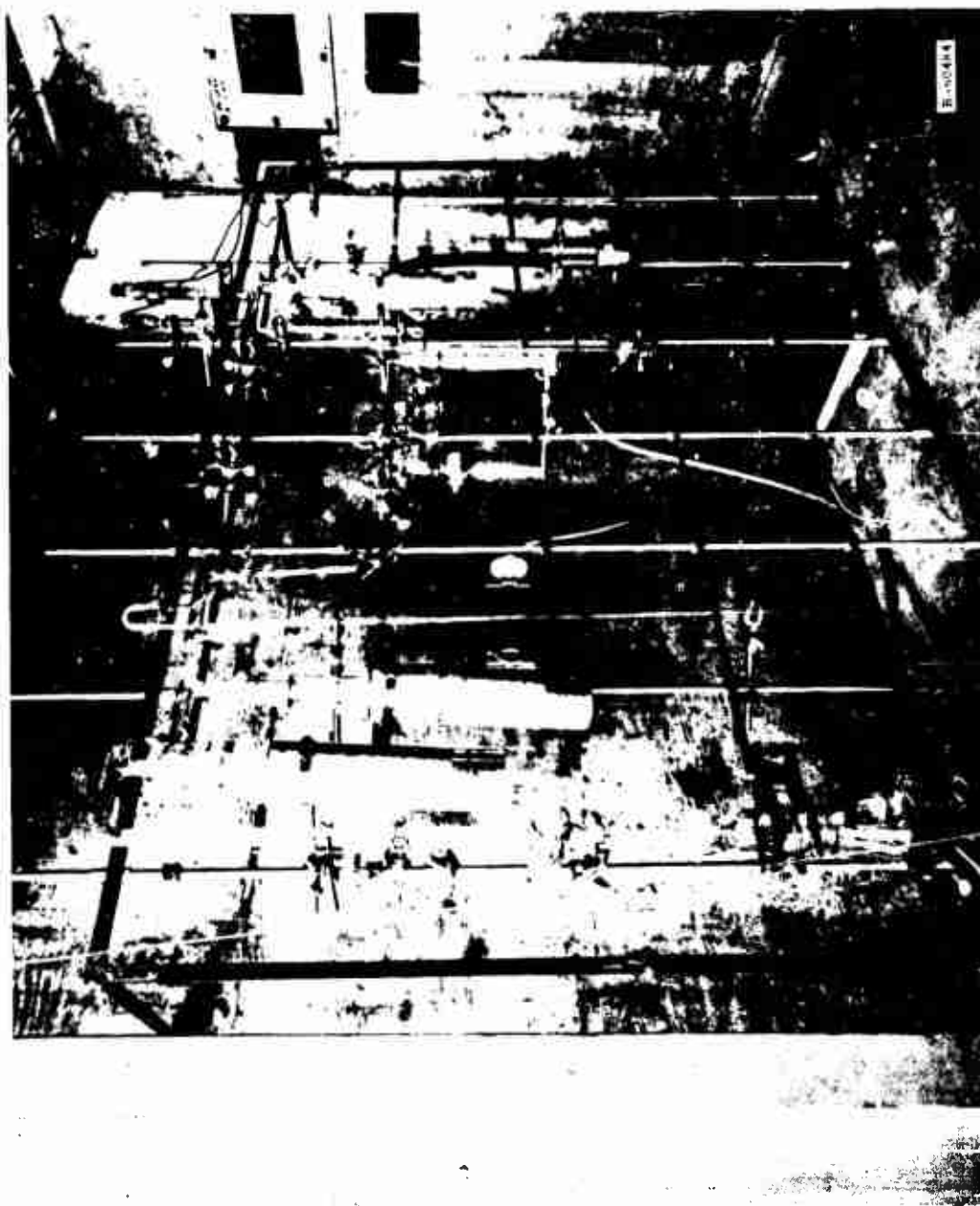


Figure 9. (C) Equipment for Drying NP

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(U) Figure 10 shows the reaction vessel and high-speed stirrer used for hypobromite oxidation of UTREZ. Also shown is a Rotavapor rotary vacuum evaporator which has been modified to permit use of dry-ice traps during solvent removal. This equipment, as well as that employed for the other indicated treatments, has been modified as necessary to ensure that the only materials in contact with the product being purified are glass, stainless steel, and Teflon. Where lubricants are required, Kel-F grease is used sparingly.

3. SURVEILLANCE

(U) Figure 11 is an interior view of a dry box which is equipped with a recirculating system capable of maintaining the moisture content below 5 ppm. The three cylindrical units are chambers in which propellant samples are stored at reduced temperatures. Each chamber consists of a metal cylinder of ca 15-in. inside diameter which is wrapped with coils of copper tubing and enclosed in an insulating coating of polyurethane foam. The top closures are made of polystyrene foam. Refrigerant is provided for the three units by a single compressor and is admitted to the copper cooling coils through individual solenoid valves. Each solenoid valve is actuated by a thermistor-controlled relay. The temperatures used in this program are 60°, 35°, and 10°F.

(U) Adequate workspace in the dry box eliminates the risk of exposing propellants to atmospheric moisture between the time of mixing and the time of storage.

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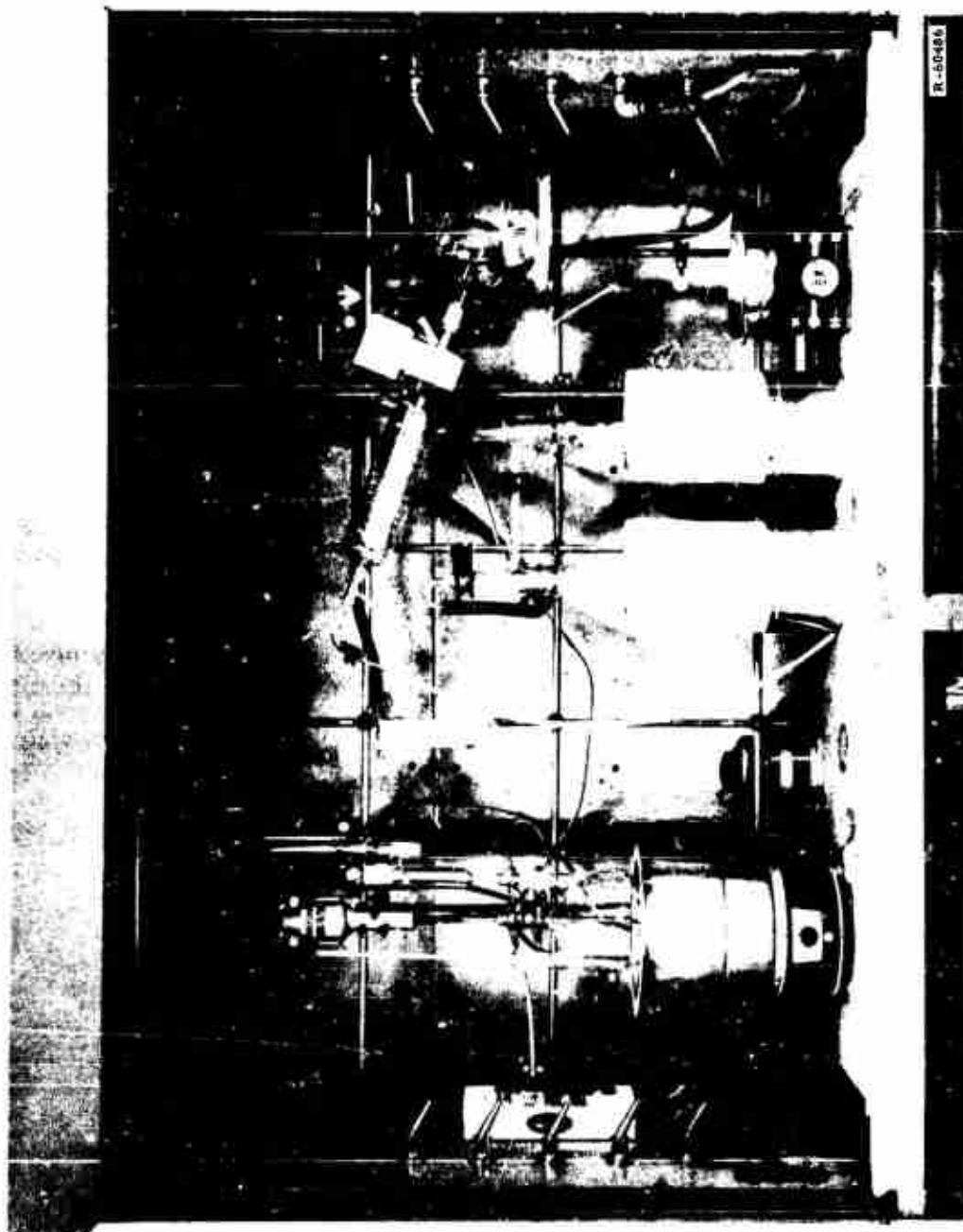


Figure 10. (U) Equipment Used in the Purification of UTREZ

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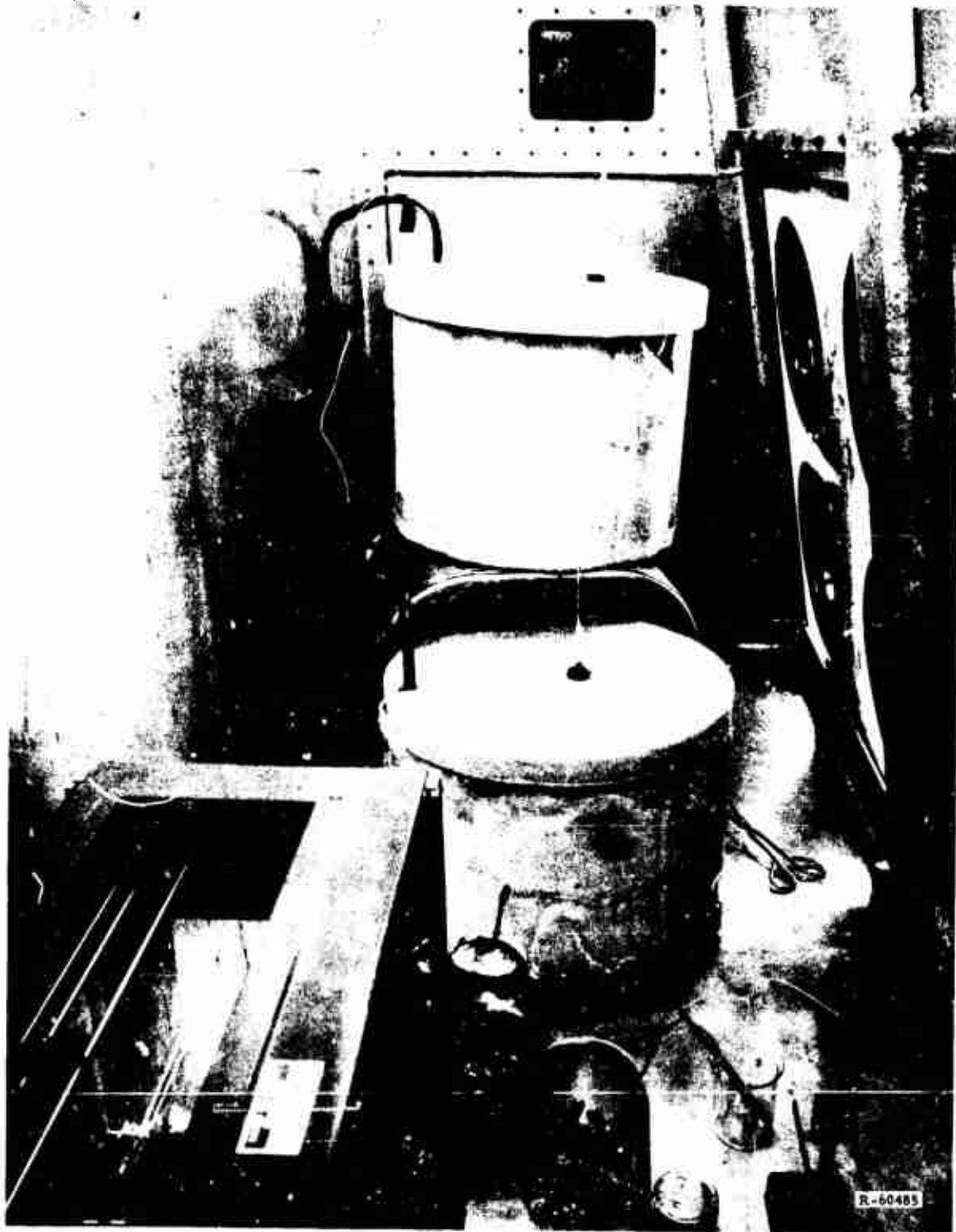


Figure 11. (U) Surveillance Facility

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report AFRPL-TR-67-236, 1 June 1965 through 30 June 1967			
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11. SUPPLEMENTARY NOTES N/A		12. SPONSORING MILITARY ACTIVITY Air Force Rocket Propulsion Laboratory Research and Technology Division Air Force Systems Command, USAF Edwards, California	
13. ABSTRACT Confidential Abstract <p>United Technology Center (UTC) has conducted a program to improve and characterize the stability of propellants containing nitronium perchlorate (NP). Major emphasis was placed on the use of uncoated NP, UTREZ prepolymer (carboxy-terminated polyisobutylene), and NTEB crosslinker (a trifunctional aziridine). Reta-coated NP was employed in limited studies. Candidate plasticizers studied included nitroparaffins and paraffinic hydrocarbons. The most promising plasticizers were HMN (heptamethylnonane) and excess aziridine (NTEB and MAPO). Increased solids loadings without impairment of stability were obtained by control of NP particle size, use of ammonium perchlorate as a supplementary oxidizer, and use of increased concentrations of aluminum fuel. The increase of propellant life obtainable by storage at reduced temperatures was studied in detail. The most thermally stable formulations exhibited exotherms beginning below 100°C and culminating rapidly in ignition. All formulations, even under mild storage conditions, lost thermal stability at unacceptably high rates. The intrinsic stability of NP is regarded as inadequate to justify further effort with this oxidizer.</p>			

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Solid propellants						
High-energy solid oxidizer						
Carboxy-terminated polyisobutylene						

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